INTRODUCTION

TO THE

ANALYSIS OF

DRUGS AND MEDICINES

AN ELEMENTARY HANDBOOK
FOR THE BEGINNER

BY BURT E. NELSON

Laboratory of the Binghamton State Hospital, and of Nelson and Lauder,
Binghamton, N Y.; Chemist to the New York State Hospitals,
The Department of Health, Board of Water
Commissioners, etc.

FIRST EDITION

FIRST THOUSAND

NEW YORK

JOHN WILEY & SONS

LONDON: CHAPMAN & HALL, LIMITED

1910

PREFACE

THE method for the proximate analysis of unknown drugs and medicinal chemicals and mixtures has not been dealt with in a general manner by any recent work in the English language; although a number of foreign treatises dealing with special classes of medicinal compounds or drug constituents have appeared within the last few years.

This neglect is no matter of wonder, as the majority of investigators are interested in the more scientific and economic problems dealing with the chemical constitution and possible methods of synthesis in the laboratory of the members of the particular class of bodies with which they are dealing, rather than in the methods of separating these from all the sorts of possible combinations in which they reach the consumer. Partial exceptions to this are the drug and chemical assays which are made for evaluation or standardization purposes, or with the object of detecting objectionable additions, and which generally have to do with known substances.

A more general work like the present, however, is intended to furnish methods by which the student or analyst who has not specialized in drug chemistry may obtain information which is often desired by Health Departments, the State, and the general public, as possibly furnishing formulæ by which unknown medicines may be duplicated, or together with occasional pharmacological experiments, indicating their relative

iii

medicinal value and safety or danger for use by a lay
public. However medical ethics may regard propri-
etary mixtures, there is undoubtedly a legitimate
place in trade for the more reliable of them, providing
of course that they do not contain any actively potent
ingredients, or containing these state clearly their names
and amounts with a suitable caution to the consumer.

Here local Health and State authorities could un-
doubtedly exercise a control similar to that found in
some foreign countries, requiring and verifying for
each such mixture sold within its territory a fairly
complete statement as to its potent contents, the
records of which might be accessible to authorized
persons, and by excluding such as were found dangerous
or obviously fraudulent.

This work is now being pursued by the Drug Lab-
oratory of the United States Department of Agri-
culture, the Council on Pharmacy and Chemistry of
the American Medical Association, and to a less extent
by a few individuals.

Quite different from these proprietary mixtures,
most of which have a trade-marked name, are the true
patent medicines which are now used extensively by
the medical profession, and which for the most part
are definite synthetic chemical compounds having
known chemical and physiological properties. These
and mixtures of these and the commonly used medicinal
substances of the pharmacopœias, which latter are
known as official medicines, are generally far the more
easy for the analyst to handle.

The following pages are intended less for the presenta-
tion of new matter or methods than for bringing to-
gether in an available form commonly used methods
and tests which the beginner, or analyst interested in

other lines of work, could only obtain from various sources.

Numerous errors undoubtedly exist, and many omissions were made necessary by the small size of the volume.

The tables of medicinal chemicals arranged in the order of their melting points, boiling points, and carbon content have proved very convenient in routine work, and these figures are largely relied upon in fixing the identity of unknown bodies.

The pages on Systematic Microscopical Drug Analysis, together with a number of the illustrations of ground vegetable drugs drawn from the microscope, are from the author's articles, "An Analytical Scheme for the Microscopical Analysis of Drugs," published serially in Merck's Report from July, 1900, to August, 1907, inclusive, and to these articles those more interested in the subject may refer, as well as to the finely illustrated works of Koch, " Mikroskopische Analyse der Drogen Pulver," " Tschirch und Osterle," " Anatomischer Atlas der Pharmacognosie," and the English work of Greenish.

As the work is intended to be elementary in nature, considerable space has necessarily been given to the methods of ordinary simple inorganic and organic analysis, and to various commonly used apparatus and operations. Credit is here given to the numerous standard American and foreign works which have been freely utilized.

CONTENTS

vii

TABLES

ix

LITERATURE

American Druggist
American Journal of Pharmacy
Archives für Pharmacie
AUTENRIETH, Detection of Poisons and Strong Drugs
BRÜHL, Die Pflanzen Alkaloide
BRICKDALE, An Introduction to Pharmacodynamics, Based on the Study of the Carbon Compounds
BURTON SANDERSON, Laboratory Handbook of Physiological Chemistry
Chemiker Zeitung
CUSHNY, Pharmacology and Therapeutics
CZAPEK, Biochemie der Pflanzen
COBLENTZ, The Newer Remedies
DIETERICH, Analyse der Harze
DRAGENDORFF, Analyse von Pflanzen
Druggists' Circular
EULER, Grundlagen und Ergebnisse der Pflanzenchemie.
FLUCKIGER and TSCHIRCH, Principles of Pharmacognosy
FRESENIUS-COHN, Quantitative Chemical Analysis
GREENE, Experimental Pharmacology
GUILDEMEISTER und HOFFMAN, Die Aetherischen Oele
HILDEBRANDT, Neuere Arzneimittel
Journal of the American Medical Association
Journal of the American Chemical Society
Journal of the Society of Chemical Industry
Journal of Biological Chemistry
KOCH, Mikroskopische Analyse der Drogen Pulver
LEACH, Food Inspection and Analysis
LENGERKEN, Handbuch Neuerer Arzneimittel
LYONS, Assaying of Drugs
MERCK's Index
MERCK, Jahresberichte

MERCK's Report

MEYER, Analyse und Constitutionsermittelung organischer Verbindungen

MULLER, Pharmacognosticher Atlas

National Standard Dispensatory

New and Non-Official Remedies, Amer. Med. Ass'n.

Pharm. Zentralhalle

Pharm. Zeitung

PICTET, Alkaloids

POZZI-ESCOT, Synthèse et Constitution des Albumenoides

Proceedings of the American Pharmaceutical Association

PRESCOTT, Organic Analysis

PROCTOR, Leather Industries Laboratory Book. (Tannins.)

ROSENTHALER, Grundzuge der Chemischen Pflanzenunter- suchung

SADTLER, Industrial Organic Chemistry

SCHMIEDEBURG, Grundriss der Pharmacologie

SCHMIDT, Die Alkaloid Chemie

SUTTON, Volumetric Analysis

TSCHIRCH, Harze und Harzebehalter

TSCHIRCH, Die Chemie und Biologie der Secrete

TSCHIRCH und OESTERLE, Anatomischer Atlas der Pharmacog- nosie

United States Pharmacopœia

United States Dispensatory

United States Department of Agriculture—Miscellaneous Bul- letins

VAN RIJN, Die Glycoside

WIESNER, Rohstoffe des Pflanzenreiches

WILEY, Foods and their Adulterants

WINTON, Microscopy of Vegetable Foods

Introduction to the Analysis of Drugs and Medicines

CHAPTER I

INTRODUCTION

THE chemical analysis of unknown medicinal mixtures entails difficulties fully as great as those found in the examination of any other class of substances, largely on account of the multitudinous array of possibly present bodies and because of the common presence of many chemically indifferent substances having no distinctive characteristics and separated with difficulty from the much smaller portions of active recognizable constituents. Also because of the extreme sensibility of many of these to such physical agents as heat, oxidation or the action of the necessary reagents. In many instances it is impossible in the present state of our knowledge to isolate and determine in a definite crystalline form, all of the proximate constituents from a mixture as we would the elements in a mineral analysis. Moreover the complete composition of most of our plant drugs is unknown.* Even granting the good fortune to be able to accomplish this, there still

---

*The term drug is here used in its more restricted sense as meaning a dried plant part in the crude state, as distinguished from pure chemical substances which may be separated from it (proximate principles) or prepared artificially.

will frequently remain the chance for considerable speculation as to the form in which some of these principles was originally introduced.

For most practical purposes, however, this difficulty is less of a drawback than might be expected because, for example, in the case of a vegetable drug, by knowing the amounts of several active constituents, we may from a knowledge of its normal composition calculate very closely the amount of crude material originally employed, e.g., having found a mixture to contain 0.5 per cent of subcarbonate of bismuth and to yield by appropriate treatment, traces of oil of cinnamon (recognized by its odor), gum, resin, meconic acid, and 0.006 per cent of crystallized morphine, and a small amount of alcohol, it is fair to suppose that the original was a mixture containing the bismuth salt mixed with tincture of opium and cinnamon water.

From this example it may also be seen that a very considerable help may be had from a knowledge of the common uses of drugs and medicines, as well as from an actual acquaintance with the sensible properties of the pharmaceutical preparations. It is often possible for a skilled observer to obtain a clue to all the bodies present in a mixture from its appearance, taste, and odor, and no drug analyst could be considered thoroughly competent who had not acquired this acquaintance by actual experience.

Frequently, too, experiments on the lower animals may be resorted to with benefit, either for purposes of directing the chemical search or for confirming the results of it. Cocaine and most of the solanaceous alkaloids possess the property of dilating the pupil of the eye when dropped into the conjunctiva, and the analysis of a mixture producing this action could

not be considered correct which did not account for
it.

The small quantity of sample available for analysis
is often another serious obstacle. While very minute
quantities of inorganic substances may be identified
with certainty, it is nearly always necessary in the
case of organic ones to have an amount of sample
which will allow of their being separated in .a pure
condition in quantity sufficiently large for allowing of
a determination of their solubilities, precipitation
and color reactions, melting or boiling points, and
frequently also of their ultimate analysis by com-
bustion in many cases.

Micro-chemical analysis and crystallography would
also seem to be particularly adapted to cope with the
problems presented here, if developed along these
lines, as they are in the case of inorganic substances,
but their pursuit would presuppose an amount of
specialized training which could hardly be expected
of the beginner. To those wishing to pursue this
branch as applied to the mineral salts and acids, the
work of Behren, " Mikrochemische Analyse," and par-
ticularly of Doctor E. M. Chamot as taught at Cornell
University, are to be recommended. Excellent articles
by the latter author appeared serially in the *Journal
of Applied Microscopy and Laboratory Methods* from
January, 1900, and extending through several years,
but are now out of print.

It goes without saying that the analyst should ob-
tain full preliminary data regarding the uses, doses
and action of unknown mixtures wherever possible,
as such information if received from reliable sources
may save many hours of useless work.

In the case of preparations from vegetable drugs,

the amounts of characteristic ingredients which may be separated from them may be not only relatively very small, but these latter are usually intimately associated with many bodies which may be common to whole classes of plants, as, e.g., tannins, resins, gums, and the indefinite group commonly called extractives, etc. Then too, the possible presence of added colors and flavors must not be lost sight of. A former belief, which empirically accredited useful medicinal properties to nearly every herb which grew, has left its record in the large number of vegetable drugs of questionable utility and whose composition and action are for the most part unknown, which are still in more or less favor in many sections. The passing of this and the contemporaneous polypharmacy of the past, and the present tendency of physicians to rely on more rational therapeutics, and to use a smaller number of single, or at least mixtures of a few definite, compounds whose composition and properties are known and whose action on the animal economy can be more accurately predicted, is now continually tending to simplify the work as far as regularly used official drugs and chemicals is concerned. Exceptions are the various serums, vaccines, and other principles derived from animal organs which are quite popular, as are numerous other products of vital activity. The investigation of these latter bodies naturally falls within the scope of bacteriology and physiological chemistry. Lastly, many preparations consist in part at least of comminuted crude drugs, usually mixed with a greater or less number of other substances. Obviously purely chemical means will here often fail to furnish means for identification, and our only recourse is the information furnished by microscopic

botany or pharmacognosy. Indeed it may be stated as a rule that to obtain good results in this work, chemistry, microscopy and experimental pharmacology must go hand in hand.

From the foregoing it will be seen that for one to thoroughly arm himself for the problems of this branch of drug work, he must needs possess a fair working knowledge of pharmacology and therapeutics, a thorough familiarity with the sensible properties of the commonly used pharmaceutical preparations, knowledge of the various proximate constituents of organic drugs, of the anatomical features by which these drugs may be identified when in a powdered condition, and finally with the methods of inorganic and organic analysis. Even with this formidable equipment he will frequently find his best efforts baffled. We are also in a position to appreciate the natural limitations of the subject matter, for as we are here chiefly interested in isolating synthetics and natural proximate plant constituents, and in identifying organized structures and simple inorganic compounds, all investigation into the composition and atomic structure of these bodies themselves, methods for their artificial production in the laboratory, and the laws governing their physical and physiological behavior, etc., belong to other departments of science.

CHAPTER II

APPARATUS AND OPERATIONS

THE room and furnishings for carrying on drug analysis will from necessity vary with the circumstances. In general it may be said that it should be equipped with suitable tables, one of them preferably low for microscopical work, a sink, and convenient water supply having sufficient pressure to operate a jet pump effectually, a fume closet having a good draught, and racks or stands for supporting small apparatus.

In the way of apparatus itself, there will be needed all of the smaller glass and porcelain pieces for carrying on general inorganic analysis, including assorted lots of beakers, flasks, evaporating dishes, crucibles, test tubes, one or more desiccating jars, the latter preferably having an attachment for exhausting the air, a good balance sensitive to one-tenth milligramme, burettes graduated to one-tenth cubic centimeter, a series of pipettes holding from one to at least ten cubic centimeters, volumetric flasks and graduated cylinders holding from ten to one thousand cubic centimeters, a water-bath drying oven and a convenient water or steam bath for evaporations, etc.

In addition to these there will be needed a number of pieces more common to organic chemical work.

Extractions in drug analysis may be applied to either solids or liquids. The former may be treated by simple maceration, by percolation, or by continuous hot percolation in one of the forms of continuous ex-

6

tractors, while the latter are generally extracted in stoppered separators or in continuously acting perforators as described below.

In extracting solids by maceration, all that is necessary is to allow the powder to stand in a stoppered flask or bottle with the solvent, occasionally agitating, and to finally remove an aliquot portion of the clear fluid for analysis.

In other cases the entire amount of solvent is occasionally removed, the residue expressed, and treated with fresh supplies of solvent until the marc is entirely exhausted.

When extracting crude drugs by the former method for assay or other purposes requiring quantitative accuracy, an allowance and correction must be made for the measured amount of menstruum absorbed by the powder, and for the volume of the latter in the total mixture, before measuring off the aliquot portion. To avoid the error of this correction it is well to complete the extraction of the powder by fresh portions of solvent as just described or to conduct the entire operation in a suitable-sized percolator (Fig. 1, *A*) to this end a small amount of cotton is forced into the neck, the contents of the macerating bottle shaken and transferred to it, rinsing out the bottle with the first portions of percolate. The percolator is now allowed to drain completely, a good-sized tuft
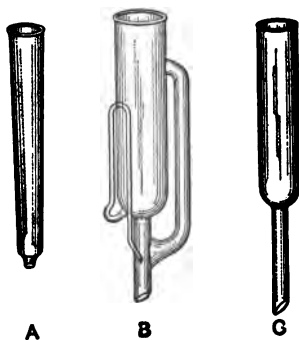
A   B   C

FIG. 1.

of cotton introduced, and the whole packed down evenly so that the last portions of menstruum run through very slowly, and the extraction then completed with fresh portions of liquid. When this process is used for the entire operation the dry powder is introduced on top of the first cotton plug and packed down sufficiently with the last one, sufficient menstruum added to soak through and thoroughly moisten the whole, the mass again packed more tightly if necessary, and the operation continued to complete exhaustion with fresh menstruum as before. As percolators, small glass syringe barrels may be made to serve.

Percolation in the manner just described undoubtedly furnishes one of the safest methods of extraction, as it requires no heat and its thoroughness can be observed, but it requires considerable time and attention and for most operations of this character has been entirely superseded by continuous hot extraction in an apparatus similar to the Soxhlet shown in Fig. 1, B.

The vapors from the liquid in the boiling flask ascend through the side tube, and after being condensed above the liquid falls back into the apparatus, penetrates the powder, which is either loosely packed in the body of the tube or loosely tied in a cotton bag, and accumulates until it reaches the level of the bend in the small siphon tube, when it is again automatically emptied back, together with its contained extracted matters, into the flask.

This apparatus is intermittent in action, the same portion of solvent remaining in contact with the powder until siphoned off. Numerous other forms are continuous acting. A convenient one of this latter type which is easily constructed is shown in Fig. 1, C. It consists of a filtering tube connected with a boiling

flask below and a condenser above. The powder to
be extracted is loosely contained in a cotton cloth or
open-ended tube, and by the side of either of these is
placed a short section of small glass tubing through
which the ascending vapors may pass.

As an amount of heat sufficient to operate any of
these forms of apparatus with solvents
boiling above 60° C. is bound to be
frequently detrimental, it will be found
advantageous to supply them with a
capacious condenser above, which is
surmounted by an air chamber and
trap.   In this way a slight vacuum
may be maintained by the jet pump,
which allows of the various solvents
boiling at a lower temperature, and
also prevents the escape of vapors from
any leaky joints should such occur.
Care must of course be used to see
that the suction is not sufficiently
strong to carry the ascending vapors
entirely through the condenser before
they have had time to become cooled.
A form of extraction apparatus which
the author has used for larger quan-
tities of drugs for special purposes, is
constructed entirely of copper and

FIG. 2.

works on the same principle.   In this the powder rests
in perforated trays.   Fig. 2.

Evaporation in the ordinary round-bottomed dishes
heated by direct heat is as a rule only suited for the
handling of inorganic bodies and others which are
known to be stable.   For most vegetable or animal
medicinal materials this amount of heat would be

entirely too severe and recourse must be had to sponta-
neous evaporation, either in a draft of air or in a des-
iccator over calcium chloride or sulphuric acid, or to
evaporation in a partial vacuum.

For the spontaneous evaporation in the air, broad
flat-bottomed glass dishes of the type known as crys-
tallization dishes or deep Petri dishes will be found
best suited, although an ordinary beaker will answer.

These dishes of various
sizes will also be fre-
quently required for crys-
tallizations.

In evaporating very
volatile liquids from
heavy liquids or solids
Dragendorff's dry-air cur-
rent desiccator (Fig. 3, B)
will be found useful. The
longer of the two tubes
in the bell jar extends
nearly to the liquid in the
dish while the exit tube
just reaches through the
cork. The air may be
drawn through the ap-

FIG. 3.

paratus by means of a filter pump or, what is pref-
erable, forced through from an air blast. In either
case the air should be first sent through one or more
towers containing granular calcium chloride, and a dish
containing this may well be kept in the bell jar, which
latter is made tight on the ground-glass base by means
of tallow or other grease. The air current evaporates
the light liquid with but little loss to the heavier bodies.
The drying materials are for the purpose of removing

all moisture from the air, which would otherwise be deposited on and in the dish owing to the cold produced by the evaporation of the light liquid. The time at which the light solvent is all blown off may usually be determined by the absence of odor in the escaping air, or by holding a non-luminous flame at the escaping jet, which will be tinged yellow as long as the air carries vapors of the organic liquid. After an operation the apparatus must be left closed until a thermometer placed with its bulb against the dish shows that the latter has warmed to the room temperature before the dish is removed for weighing, where this is desired. This apparatus and operation are perhaps most frequently used for evaporating light petroleum ether from volatile oils, camphors, etc., which have been extracted by it.

In the case of non-volatile bodies, e.g., fats, resins, etc., extracted by these light liquids, this arrangement is of course unnecessary.

In all processes of open evaporation, the volatile liquid is of course lost. In order to recover and save this for study or re-use and also frequently for the purpose of saving valuable time, **distillation** is resorted to, although the fixed residues left behind are seldom in a crystalline condition, as they may be after slower evaporation.

In the case of stable liquids, leaving no residue or at any rate a fairly stable one, or in the case of solvents with boiling points below 60° C., a distilling flask connected with an ordinary Liebig's condenser or worm (Fig. 4) may be employed. The apparatus may also be used for separating a mixture of liquids by fractional distillation or by introducing a distilling tube carrying a thermometer between the flask and con-

denser. The liquids boiling between different tem-
peratures are caught in separate receivers, after which
the distilling operation is repeated one or several times
until each of the different fractions boils at a constant
temperature. For this purpose another flask is selected
capable of holding about double the largest fraction,
and the first fraction which previously came over is
introduced and distilled into its original receiver until
the highest temperature at which it previously boiled
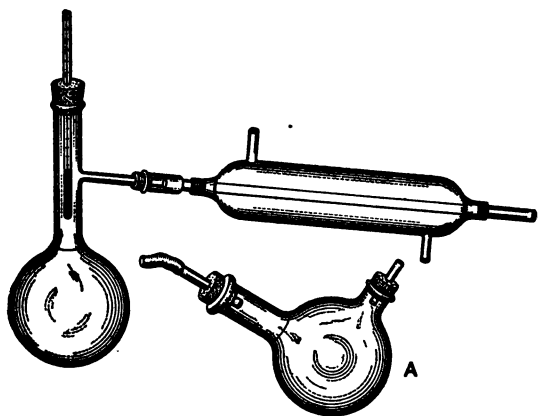
FIG. 4.

is reached. The heat is temporarily removed and the
second fraction likewise introduced into the boiling
flask along with any residue which may have been left
behind from the first fraction, and similarly treated
and so on through all of the fractions. By this treat-
ment it will be noticed that the fractions gradually
tend to accumulate around certain boiling temperatures,
and when the operation is complete, each liquid will
have distilled completely at its particular degree of

heat, known as its *boiling-point*. In the separation of volatile solvents from medicines, two distillations are generally sufficient. The bulb of the thermometer should be opposite the outlet into the condenser. In the case of liquids which do not boil at ordinary pressure without decomposition or of those holding organic solids in solution, which is most frequently the case in this work, recourse must be had to distillation in a partial vacuum. For this purpose some arrangement similar to that shown (Fig. 4, *A*) will be necessary. Suction is supplied by a good jet pump supplied with water pressure or by means of a pump driven by a motor or by hand.

The apparatus requires to be made of strong glass or brass tubes and the connections are conveniently made with good rubber and glass, or lead tubing which does not collapse as does ordinary rubber. In any case it is well to place an air chamber and gauge between the pump and tubulated receiver to equalize the suction and retain any water which might be drawn in from a suddenly diminished pressure in the water mains, and to indicate the vacuum being used. Generally speaking the higher the vacuum the better— 24 to 29 inches. In this way liquids may be distilled at temperatures far below their normal boiling points, and by never allowing them to become warmer than 60° C., no harm will be done to sensitive compounds dissolved in them. It will frequently happen that heavy liquids can be better separated by fractional distillation in a partial vacuum. For this purpose a receiver arranged similarly to the one shown in Fig. 5 may be used, where by turning the central spindle each receiver may in succession be brought under the end of the condenser as the boiling-point

changes. The vacuum for this fractional work must be practically constant. Distillation with streaming steam is another operation which is often resorted to for separating volatile bodies from others. For this purpose a stream of live steam is continually delivered into the bottom of the boiling flask containing the bodies and the resulting water condensed along with the desirable portions.

Fig. 5.

The flat-bottomed Erlenmeyer type of flask is the one most convenient for most drug work, as it allows of drying and weighing the residue *in situ*. In saponifications, esterifications and some other operations where the boiling fluid requires to be retained rather than separated, the boiling flask is connected with the lower end of the condenser, placed upright as in continuous extractions.
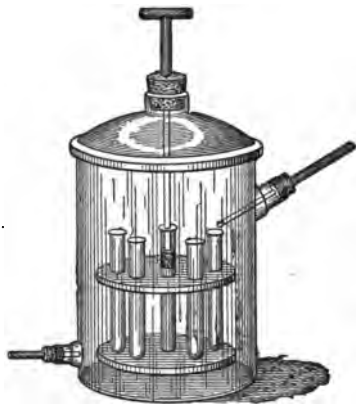
Drying is of course necessary before the amount of any separated solid can be determined by weighing.

Inorganic salts and salts of mineral acids may be dried in an air bath or water bath oven at from 100° to 110° C. with safety, but most vegetable bodies are best dried at from 80° to 85° C. A few sensitive vegetable, and nearly all animal products, however, are best dried in a desiccator over sulphuric acid or in a vacuum drying chamber. The vacuum chamber may also be used for evaporating small quantities of solutions. As in

the case of the distillation of sensitive bodies, the higher the vacuum and the lower the temperature the better. In any case the drying is continued until between successive weighings the loss of weight is insignificant.
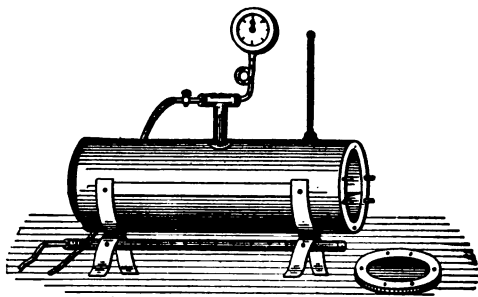
FIG. 6.

Of the various types of vacuum drying ovens the one shown in Fig. 6 is perhaps as useful as any.

The Boiling Point of a pure liquid is, as before stated, a physical constant which serves for its identification. This may be determined during distillation as previously described or in the arrangement shown in F g. 7, *A*. In the former case a correction must be applied for the thread of mercury if it extends beyond the hot vapors in the flask. When as frequently happens the amount of liquid is to small to allow of these methods being used, the device shown in Fig. 7, *B*, will give results usually within three degrees of correctness. It consists of a small closed tube about two or three millimeters in internal diameter, containing a very fine capillary tube fused together near one end.

The liquid to be examined is introduced into the bottom of the larger tube and the capillary somewhat

heated and dropped into it open end downward. On the capillary cooling a small thread of the liquid is drawn into it. If the larger tube be now attached to the bulb of a thermometer and the whole heated slowly in a beaker of sulphuric acid to act as a bath, a small chain of bubbles will be formed in the capillary as the boiling-point of its contained fluid approaches. The formed vapor will empty the capillary, when on cooling it again fills and allows of a repetition of the test. The beginning chain of bubbles is taken as the boiling-point. One or two drops of liquid is sufficient for a test.

A   B   C
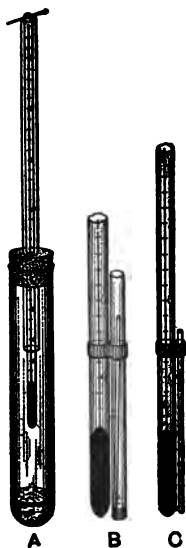
Fig. 7.

Sublimation or the dry distillation of volatile solids is an operation which is sometimes useful in drug work, but on account of the heat necessary, it is seldom safe to resort to it except for the purpose of separating a known volatile substance of stable composition from a known stable residue or a residue which is not to be examined further for sensitive bodies.

A form of sublimation cell is convenient which allows of the application of a partial vacuum, in which volatile substances sublime more easily. It consists of a broad shallow brass cup having a ground flange on which rests a tubulated glass plate cover. The cup with its contained material is best heated on an iron plate and the cover is kept cool by means of a moistened disk of filter paper or blotting paper while in use. A simpler contrivance consists of a watch glass contain·

ing water and resting on an ordinary tin box. By previously weighing the watch glass and again after the deposition of the dry sublimate, the results in some cases, as in working with caffeine, may be made quantitative. At ordinary pressures the subliming point is a constant.

Filtration is generally accomplished by papers supported in ordinary funnels as usual, although the Gooch filter is convenient when precipitates or residues are to be dried for weighing and then afterward ignited. In filtering off gummy or resinous residues, as well as those containing fats, oils, etc., it will often be advantageous to introduce some ground pumice or kaolin and to shake or stir well for some time in order to tangle up the very fine particles of sticky material before pouring the mixture upon the filter.

When small quantities of active bodies are being washed out of a dish or flask containing resinous or other sticky materials, the first portions of the aqueous solvent are best first decanted through the filter, and the resinous residue again worked up with its original solvent, a little water being gradually worked in, and finally more water added until precipitation of the resinous mass again occurs. The organic solvent is again evaporated and the successive aqueous extracts passed through the filter. In this way only can the active bodies be entirely washed out of such sticky residues.

In filtering hot solutions intended to deposit crystals on cooling, it is well to use a hot covered funnel whose beak has been broken off, and for some purposes a hot water jacketed funnel is desirable.

For the decolorization and other purification of some colored solutions which are intended to be crys-

tallized, it is common to shake or stir them for some time with thoroughly purified animal charcoal before the final filtration, but here it must be borne in mind that the charcoal may retain valuable bodies and it must consequently be afterward examined. A creamy suspension of aluminum hydroxide in water is also often valuable for a similar purpose, as well as for retaining finely suspended resinous precipitates on the filter, but the same precautions regarding the retained bodies must be kept in view.

In filtering off voluminous precipitates for washing, e.g., those produced by normal and basic lead acetates in vegetable extracts, the operator will usually save time if after the first lot of filtrate has passed, he pierce the tip of the filter, wash the precipitate into the original flask, and shake it again with water containing a few drops of the reagent, before the final filtration and washing.

Separations by Immiscible Solvents, as, e.g., oil and water, are perhaps as commonly employed as any operations in drug analysis. For this there will be needed one or more separators or separating funnels. These will best be of the form shown in Fig. 8, and will preferably range in size from 50 to 250 cc., the 100 cc. size being perhaps most commonly used.

If the stems are cut and ground off diagonally quite close to the stop cock they are much more convenient to use. The cocks and glass stoppers are best kept tied loosely with strings and slightly greased when not in use, to prevent breakage from dropping, or from the cocks becoming cemented into their seats.

An ordinary narrow-beaked funnel may be made to answer for a separator by grinding the end of a stout glass rod into its neck with emery and water. When

left standing the rod must be supported by a perforated cover. For many small operations too a very convenient separator may be constructed in a similar manner from a pipette (Fig. 9). In filling this, suction is applied by means of the mouth, either directly to
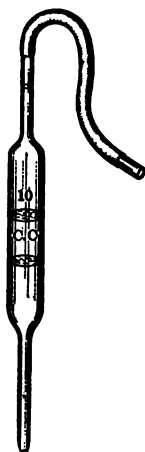
FIG. 8.   FIG. 9

the upper end or through an intermediate section of rubber tubing.

All these forms are convenient for drawing off heavy liquids from below immiscible lighter ones as, e.g., chloroform from water. When the object is to separate a lighter top fluid as, e.g., ether from water, these same forms will answer, the lighter liquid being poured off through the top opening *after* drawing out the heavier one below and closing the cock as the last drop emerges.

Frequently, however, and especially when dealing with small quantities of liquids, it will be found fully

as convenient to use a narrow test tube or cylinder and to remove the supernatant fluid by pouring off, or by means of a bulbed pipette. Some operators prefer a wash bottle arrangement where the exit tube is forced in until it is very slightly above the line of demarcation between the two liquids. I have never found this type satisfactory.

In using any of these forms of separators, sufficient time must be allowed for the two immiscible liquids to completely separate and form a sharp line of demarcation. Where an unfortunate emulsion occurs, as will sometimes happen, no sharp separation can take place. The emulsion may be often broken up by warming the separator in warm water or perhaps by introducing more of the lighter solvent, or by introducing a small quantity of alcohol directly into the emulsified mass by means of a pipette. All of these and similar expedients must be tried before giving up. It will also often suffice to pour the whole onto a wetted filter when the aqueous solution will run through, leaving the upper organic one in the paper, but where chloroform or some other immiscible solvent heavier than water is being used the filter had best be wet with this instead of water, and effort made to retain the upper aqueous liquid in the filter.

As before stated, this operation is used chiefly for extracting organic bodies from aqueous solutions by means of immiscible organic solvents, or vice versa. The method, first perfected by Stas-Otto and afterward elaborated by Dragendorff, depends upon the fact that organic acids and other acidic bodies, when combined with alkalies in aqueous solution, are for the most part insoluble in the various organic solvents which are more or less immiscible with water as, e.g., chloro-

form, ether, benzene, acetic ether, petroleum ether, carbon tetrachloride, carbon disulphide, etc., but are liberated by acidifying the aqueous solution with a mineral acid, and may then be removed by shaking the aqueous solution with a suitable one of the above solvents, allowing the two solutions to completely separate, and repeating the operation a number times.   In like manner alkaloids and other organic basic sub-stances are liberated by a slight excess of mineral alkali from their acid aqueous solutions, and may be similarly separated. It will frequently happen, however, that a substance is soluble in both the aqueous and organic solvent and in these cases they may often be separated by "salting out" the aqueous solution, i.e., by saturating it with a mineral salt, usually common salt or sodium sulphate, before proceeding to extract it with the organic solvent.   If the aqueous solution is to be afterward examined for its mineral constituents, the chemicals used for salting out must be of known purity and due allowance made for them in the final calculation.

FIG. 10.

Instead of using the stoppered separators just described, the same principles may be followed and objects accomplished by conducting the operation in an apparatus working on the principle of the one shown in Fig. 10, and commonly spoken of as a per-forater.   Here the light immiscible liquid vapors ascend to the condenser, the liquid falls back through the inner funnel tube until a column sufficiently high to balance the heavier aqueous liquid has accumulated, then

rises through the latter to overflow again into the boil-
ing flask in which it leaves its dissolved bodies.   With
liquids heavier than water a special overflow tube must
be placed inside the body of the perforator and a small
portion of the heavy immiscible liquid first introduced
for the purpose of sealing the exit tube from the aqueous
solution, which is afterward poured in.   By arranging
two or more perforators above each other it may be
so managed that the bodies extracted from, say, an acid
aqueous solution in the upper one, are retained by an
alkaline aqueous solution in the one or more lower
ones and vice versa.   Instead of making these extrac-
tions and separations from the solutions, it will fre-
quently be necessary or desirable to evaporate the
aqueous liquid with sand, pumice, or salt, as, e.g.,
the residual salt solution remaining after extraction
by immiscible solvents from the salted-out solution,
stirring the mass well as dryness approaches, and then
to extract the dried residue distributed over the sand
or salt grains with an organic solvent which will not
attack the latter, in one of the forms of extraction
apparatus previously described.

Crystallization and in many cases fractional crys-
tallization, will be necessary before the majority of
plant principles, etc., from the residues left by the
evaporation or distillation of the various organic sol-
vents can be obtained in a condition sufficiently pure
to allow of their identification by means of their melt-
ing points, color reactions, elementary analysis, etc.
This is an operation which is capable of furnishing
much valuable information in the hands of a skilled
operator, but it not infrequently requires the expend-
iture of a considerable amount of time and in some
cases is very difficult of execution, as the bodies sought

may persistently retain portions of the extraneous
materials which will prevent their separating in definite,
pure, geometrical forms.   The operation is conducted
in the crystallization dishes or beakers previously
described.

The solvents from which crystallization of these
bodies is usually effected are water, alcohol, methyl
alcohol, acetone, chloroform, ether, acetic ether, glacial
acetic acid, benzene and petroleum ether.   A number
of preliminary trials are usually necessary for determin-
ing the most suitable solvent.   Small quantities of
the material under investigation are treated in small
corked tubes with small portions of the various sol-
vents.   Those in which solution takes place readily
are temporarily set one side and the others heated in
a water bath.   Those in which solution occurs on
warming are now likewise set one side in a quiet place
to cool slowly while the remainder are treated with
a larger quantity of their original solvents, and again
heated to see if solution will not occur.

The solvent from which crystals form best and in
the largest quantity is usually selected for handling
the entire amount, the several trial portions being
again freed from their solvents by evaporation and
added to the main residue.   It will, as before stated,
often happen that crystals will not form well from
any of the solutions.   In these cases it is well to allow
all of the tubes to stand uncorked in a quiet place and
see if upon evaporation and consequent concentration
of the solutions some success may be had.   When
none of these measures succeed the solutions are very
gradually treated with some of those liquids in which
the substance has been found to be insoluble or very
difficultly soluble, until a slight permanent turbidity

results, and then allowing the mixture to again stand quietly for some time, perhaps with the further addition of more of the poor solvent. The two liquids used must as a rule be miscible with each other, but there are marked exceptions to this rule. A small quantity of crystals from the most successful of these trial operations is preserved for introducing into the main lot just as it is about to crystallize. This "seeding" operation greatly promotes the second crystal formation. Generally speaking, the solvent in which the substance is least soluble while cold and most soluble while warm will prove the best. Where a substance starts to dissolve readily, but leaves a residue which is more or less insoluble, the operator should filter off the first solution while hot, and treat the remainder separately, as the cause of the irregularity is probably impurities in the substance or the fact that there are two or more bodies having different solubilities present. In all filtrations after heating, care must be taken to use a hot stemless funnel and to avoid cooling during the operation, as otherwise the materials may crystallize out on the funnel and filter. . After the first crop of crystals is obtained they are thrown onto a filter and slightly washed by means of a filter pump with an appropriate liquid, after which the mother liquor is again allowed to evaporate slowly, when another crop of crystals will be obtained. The crystals may be allowed to drain or even dry on a porous plaster-of-Paris slab or on filter or blotting paper. The final liquor and wash liquids contain as a rule most of the impurities. Where two or more substances are present in the same solution, they may, on account of their different solubilities, usually be separated by fractional crystallization. In this operation the different lots

of crystals are filtered off and washed as they are formed during the gradual evaporation of the mother liquor. Afterward the process may be repeated with a fresh lot of the clean solvent, somewhat after the manner of a fractional distillation. Even after the utmost care, however, many plant principles will refuse to crystallize.

The Melting-point is a physical constant upon which the drug analyst is often forced to rely largely as a means of identifying separated organic bodies, both because of the reliability of its indications when the substance is pure and the operation properly conducted, and because of the small amount of material necessary for a test, which is often a factor of considerable importance. The arrangement shown in Fig. 7, *C*, is the one most frequently employed, although the results obtained by it may vary slightly from those obtained in a different way from larger quantities of material.

It consists of a section of fine glass tubing, fused together at its lower end and fastened to a thermometer by means of a small elastic band or platinum wire, the whole being immersed in a water or sulphuric acid bath. A small portion of the material is introduced into it by means of a steel pen point or other similar implement, and the whole heated slowly until the loose mass is seen to melt and run together, when the temperature is noted. To secure reliable results the material must be completely purified and dry. Impurities, as a rule, lower the melting point, although with many exceptions. In Table 3 are given the melting points of some of the common medicinal chemicals.

Color Reactions are common tests by which the identity of a separated organic body is arrived at, and here, as above, small quantities of impurities are apt

to give misleading results. In applying them, a small quantity of the dry substance or the residue left by the evaporation of a drop of the solution is usually treated directly on a white slab or glass plate placed over a white paper with the reagent employed, with or without the employment of subsequent heating. The reaction, as a rule, produces a play of colors, and here their intensity as well as their sequence must be observed. In other cases the reagent may be added directly to the solution or the dry substance added directly to the reagent in a test tube. Frequently contact tests between the solution of the substance and the reagent are employed.

Precipitation Reactions are also frequently employed, either directly for purposes of identification, or for forming double compounds whose melting point is characteristic, or for making general separations during the course of the analysis proper. Alkaloids are especially characterized by these reactions.

Solution of solid medicines preparatory to treating them with precipitants or other reagents, or for purposes of separation, is usually primarily effected in either water or alcohol of various strengths, which dissolves the majority of medicinally active bodies except fats and a few inorganic chemicals like the basic bismuth salts, cerium oxalate, etc. Further solution of the various organic bodies for purposes of separation is usually effected by petroleum ether, benzene, chloroform, ether, acetic ether, etc.

As a rule the inorganic chemicals are but slightly affected by most of these latter solvents, and it is often necessary to utilize this fact in separating the two great classes of bodies, in dealing with small amounts of material which do not admit of dividing the sample.

These solvents may be applied directly by shaking or triturating the substance with them, by shaking out the solution in a separator, or by extracting the dry material in one of the forms of continuous extraction apparatus.

Frequently it is not possible to sharply separate the organic from the inorganic portions of a mixture by means of solvents, as many salts dissolve appreciably in strong alcohol, etc., while a few, such as potassium iodide, the ammonium salts, ferric chloride, lead acetate, bichloride of mercury, zinc chloride, etc., are readily soluble in this liquid. In such cases it is usually possible to complete the separation by again taking up the residue left by the evaporation of the alcoholic solution with water, to extract the organic bodies with some other immiscible solvent in which these only are soluble, and finally to unite the aqueous solution with the original residue insoluble in alcohol for the inorganic analysis. Where no valuable organic materials are present the inert ones are frequently simply gotten rid of by "ashing" the mass or by digesting it with hydrochloric acid and potassium chlorate or nitric acid.

Microscopical Analysis offers the only way of attacking the residues of organized material consisting of comminuted crude drugs, insoluble in all simple solvents, which frequently remain after any of our treatments, and in fact some medicines consist almost entirely of these substances. Even recognizable traces of plant parts will often furnish a valuable clue to the nature of the material which may have been extracted from them. For this work there will be needed a microscope and a few additional accessories. The former need not necessarily be of the more elaborate type, as some of

the complex mechanisms of these are not only un-
necessary, but are actually in the way.   In general
it may be said that a good smooth-working stand
having a one-sixth- or one-fourth-inch (4 to 6 mil-
limeter) and a two-thirds- or three-quarters-inch
(16 to 18 mm.) objective, and a one- and two inch
ocular is all that is required.   Such a stand is shown
in Fig. 11.   It is sometimes desira-
ble that it be provided with a sub-
stage ring for carrying the lower
prism of a micro-polariscope, and
a double or triple nose-piece is
convenient, but a complete sub-
stage or mechanical stage and con-
denser is unnecessary unless the
instrument is also to be used for
bacteriological and other purposes.
The only accessories needed are a
number of one-inch by three-inch
glass slides, and three-quarter-inch
round cover glasses.
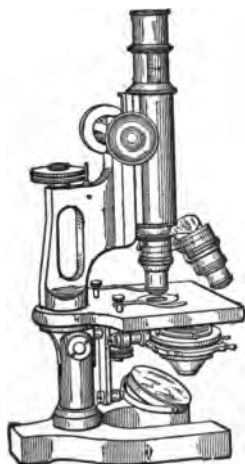
FIG. 11.

A very useful adjunct, which,
however, requires considerable time
to arrange properly, consists of a
cabinet containing small vials of typical samples of all
the important ground drugs together with permanently
mounted and classified microscope slides of each of
them.   These serve for comparison with the unknown
drug which may be found in a mixture.   To make use
of these tests a small portion of the powder is placed
in a drop of water contained in the middle of one of
the glass slides, covered with a cover glass, which is
pressed and rubbed down slightly, and the whole
examined first under the low- and then under the high-

power objective. This water mount will serve for
showing starch granules and other cell contents, and
also allows the use of such micro-chemical reagents
as iodine solution for starch, iron solution for tannins,
etc., but the anatomical structure of the cells them-
selves is perhaps best shown by mixing the powder
with a drop of a mixture of equal parts of alcohol,
glycerin, and hydrated chloral, covering as before with-
out pressing down the cover glass, and boiling two or
three seconds over a small flame. This treatment
dissolves starch and other cell contents, bleaches and
clears the tissues, and leaves the mount in a condition
interesting to examine. Starch granules from various
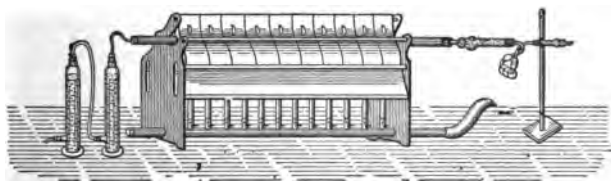
FIG. 12.

plants, besides varying widely in shape and size, often
show characteristic dark crosses when viewed between
the crossed Nicols of the micro-polariscope. After
obtaining an accurate idea of all the anatomical ele-
ments found, especially the measure of certain of them
with the eyepiece micrometer accompanying the micro-
scope, reference is made to the analytical key in Chap-
ter IX, for the name of the drug. A typical slide of
like fineness and mounted in the same manner, is then
compared with the powder under examination. It
must be borne in mind that other materials mixed
with these powder residues may alter the color and

other appearances somewhat, but they do not change the cellular structure.

Elementary or Ultimate Analysis of separated organic materials frequently furnishes final facts for identification. This operation is so important a one, that a separate chapter is reserved for its consideration. The type of combustion furnace shown in Fig. 12 is a very satisfactory one to use.

CHAPTER III

ULTIMATE INORGANIC ANALYSIS

THE analysis of medicines which are wholly inorganic
in their composition, or of the inorganic portion of a
mixture, requires no special knowledge other than that
taught in a general course in qualitative and quan-
titative analysis, and outlined in the following pages,
and the experienced operator may follow his own dis-
cretion as to methods. In the former case the analyst
proceeds at once to the systematic separations, while
in the latter the accompanying organic matters must
first be gotten rid of. Mineral matters may be de-
tected when present by completely incinerating a small
portion of the mass on a strip of platinum foil, or better
still, in a hard glass tube through which a slight stream
of oxygen gas is passed, when any residual ash or in-
organic sublimate will consist of the mineral matters,
except for ammonium salts, etc., which are of course
volatilized by this treatment. In the latter case a por-
tion of the material is heated in a test tube with a slight
excess of sodium hydroxide solution, when ammonia will
be recognized by its odor or by rendering blue moist-
ened red litmus paper held at the mouth of the tube.
By distilling a known amount of the material into
tenth normal acid solution until the distillate ceases
to be alkaline and titrating back with tenth normal
alkali, the amount of the ammonia may be determined
and from this amount of the ammonium salt found

31

calculated. Each cc. of acid so consumed is equal to 0.0017 g. of ammonia.

In the analysis of crude plant drugs one usually contents himself with the analysis of the ash left on igniting a weighed amount of the material at a low red heat, extracting the charred mass with water, incinerating the carbonaceous residue completely at a higher heat until it is uniformly grayish-white in color and free from black specks or other carbonaceous material, evaporating the previous watery extract to dryness in the tared crucible with this residue, and finally again igniting moderately, after which the crucible and contents are allowed to cool in a desiccator for weight.

In the case of unknown mixtures, however, this simple means of destroying the organic matters will not suffice, as many of the inorganic compounds used in medicine are volatile at a red heat, notably salts of ammonium, mercury, arsenic, antimony, zinc, etc., and here it is always safer to destroy the organic materials by digesting the mass with a mixture of hydrochloric and nitric acids on a sand bath until the organic material is completely destroyed, adding more nitric acid and possibly also hydrochloric acid if necessary. This operation should of course be performed under a hood having a good draught or out of doors. The excess of acids is finally evaporated on a water or steam bath, and the residue taken up with water. Compounds of arsenic, antimony, mercury, etc., are often conveniently tested for at first by Reinsch's test. An acidified (hydrochloric) solution of the material is boiled in a test tube with a strip of bright pure copper foil when in the presence of these (and a number of other metals) a grayish film will be deposited on the

copper. If the latter is now washed, dried, rolled up, introduced into an open-ended hard glass tube and held at an angle of about forty-five degrees in a flame, which is directed under the portion of the tube containing the copper, the metals will sublime and be deposited beyond the foil in the cooler portions of the tube, first the antimony as a grayish, almost always amorphous film, the arsenic in brilliant octahedral crystals which in the case of very small quantities may require a lens for seeing well, and finally the mercury as a grayish micro-globular film, in which globules of the metal may be produced by rubbing. Other confirmatory tests should of course be applied. In the absence of any of these and of ammonium salts, it is sometimes permissible to free the inorganic compounds from the organic in mixtures by ashing.

Where the quantity of the sample is too small to allow of using a separate portion for the determination of mineral ingredients, the mixture is first extracted with organic solvents as already described (page 27), taking care not to introduce any unknown mineral matters, and the other inorganic constituents recovered as above, alcohol, sugars, glycerin, gums, etc., being determined as described later.

It must not be forgotten that by ignition all of the alkali and alkaline earth salts of organic acids are of course converted into carbonates, which is also true of nitrates, etc., when ignited with carbon, or what amounts to the same thing, with organic residues, but in the latter case as also with chlorates, bromates, etc., deflagration will ensue, and so give evidence of the nature of the acid present. Organic salts of most of the heavy metals leave the oxides after strong ignition.

By whatever method obtained, the mineral matters are finally secured in aqueous solution by the aid of hydrochloric acid, or in the presence of silver, mercurous, and lead salts, nitric acid, heating if necessary to insure complete solubility. The liquid is then divided into two aliquot portions, generally three-fourths and one-fourth, for the estimation of the bases and acids respectively, or when desirable into a third portion to be used for qualitative tests.

SEPARATION AND DETERMINATION OF THE METALS

Separation of the Metals into Groups

1. Add hydrochloric acid to the larger solution if not already acid, which will precipitate silver if present as white silver chloride, mercurous salts as white mercurous chloride, or if the solution is fairly concentrated and cold, perhaps also lead chloride, which latter will, however, redissolve in an excess of the hot solution. The precipitate of washed silver chloride is dried, the filter incinerated in a tared crucible, the precipitate added, and ignited carefully until it just begins to fuse at the edges, allowed to cool in a desiccator, weighed and the correction for the previously determined ash of the filter applied; 75.3% of the weight of the precipitate is silver. Or volumetrically, fuse the washed precipitate, well mixed with pure sodium carbonate, in a porcelain crucible at a high heat, allow to cool, wash the silver button with water, dissolve by the aid of heat in nitric acid, neutralize with pure calcium carbonate, and titrate the solution with tenth normal sodium chloride solution using potassium chromate as

indicator, until the red color of silver chromate just disappears, each cc. of the solution being equivalent to 0.0107 g. of silver.

Qualitative Tests: Soluble silver salts are precipitated white by hydrochloric acid or soluble chlorides, which precipitate is soluble in ammonium hydroxide. Potassium chromate produces a red precipitate of silver chromate.

The mercurous chloride when present seldom represents the entire amount of mercury, so it is well after filtering off the precipitate produced by hydrochloric acid to boil it with nitric acid, add water and finally wash it on the filter with hot water, the filtrate and washings, containing the mercury now as a mercuric salt, being added to the main solution.

2. Warm the filtrate and washings from the hydrochloric acid precipitate to about 75° C., and treat the solution slowly with hydrogen sulphide gas which has been purified by being caused to bubble through water containing some ammonium sulphide, until the solution smells strongly of the gas, stopper the flask and allow the whole to stand in a warm place for some time, adding more hydrogen sulphide if the odor becomes weak, and finally filter and wash the precipitate, if any, with water containing a little hydrogen sulphide. Any precipitate produced may consist of free sulphur only, which is pale yellow, combustible, and soluble in carbon disulphide, or of the sulphides of the metals of the sixth group, viz., gold (brown), platinum (brown), arsenic (yellow), antimony (orange), or tin (brown or yellow), and of the fifth group, viz., lead (black), mercury (black), bismuth (black), copper (black), or cadmium (yellow), silver having of course been previously removed if present.

The precipitate is washed into a test tube or flask with yellow ammonium sulphide solution, the flask corked and digested in the hot water bath two or three times with fresh portions of yellow ammonium sulphide, filtered off, and the ammonium sulphide solutions united. The washed insoluble residue may consist of the sulphides of any or all of the metals of the fifth group. Examine by 6.

The ammonium sulphide filtrate may contain any or all of the metals of the sixth group. It is to be treated with an excess of hydrochloric acid, which, besides free sulphur, will again precipitate the metals of the sixth group as sulphides, with possibly accidental traces of copper or cadmium. Examine by 5.

The filtrate from the original hydrogen sulphide precipitate is treated with an excess of ammonium hydroxide and ammonium sulphide, a little ammonium chloride being also desirable, the flask corked and allowed to stand some time. A precipitate may consist of the sulphides of the metals of the fourth group, viz., iron (black), zinc (white), manganese (flesh-colored), cobalt (black), or nickel (black), or of the hydroxides of the metals of the third group, viz., aluminum (white), or chromium (greenish). Wash the precipitate with water containing a little ammonium sulphide, dissolve in hydrochloric acid, boil with a few drops of nitric acid, filter from the separated sulphur, and examine the solution according to 7.

3. Treat the filtrate and washings from (2) with more ammonium chloride and an excess of ammonium carbonate and allow to stand until the precipitate has completely settled. Filter and wash with water containing more ammonium carbonate. The precipitate contains the metals of the second group except magne-

sium, as carbonates, viz., calcium, barium, and stron-
tium.   Examine by 8.

4. Evaporate the filtrate and washings from (3)
to dryness and ignite cautiously until all of the ammo-
nium salts are driven off.   Take up the residue, which
may contain magnesium, potassium, sodium or lithium,
with water and examine by 9.

SEPARATION OF THE MEMBERS OF GROUPS

5. Boil the precipitate consisting of the sulphides
of the metals of the sixth group with strong hydro-
chloric acid, decant the solution into another test
tube or flask and wash the residue, if any, with water,
which is also added to the acid solution.

The residue, which, besides free sulphur, may contain
gold, platinum or arsenic, is dried, introduced into
a small trough or boat of porcelain or glass, which in
turn is introduced into a glass or porcelain combustion
tube, and the tube around the boat heated to redness
while a slow stream of chlorine gas is allowed to pass
through it and a U-tube containing water beyond, the
flame being finally lighted under the entire length of
the tube to guard against any sublimate of arsenic
chloride remaining deposited behind the U-tube.   After
cooling the boat is carefully withdrawn, the contents
if any dissolved out by boiling with strong nitro-hydro-
chloric acid, the solution evaporated to dryness on the
water bath and taken up with water.

Neutralize any free acid if present with very dilute
potassium hydroxide solution, add an excess of strong
solution of potassium chloride and enough strong alcohol
to make the whole of about 80% alcoholic strength; allow
to stand several hours, collect any precipitate of potassium

platinic chloride which may be formed on a very small tared filter; wash with 80% alcohol, dry and weigh; 40.1% of the precipitate is platinum. Or ignite the precipitate strongly in a porcelain crucible with a little oxalic acid, wash the residue several times with water by decantation, again ignite and weigh as metallic platinum.

Qualitative Tests: Insoluble in all simple acids, soluble in nitro-hydrochloric acid, not precipitated by ferrous sulphate, but yielding a double salt insoluble in 80% alcohol with potassium salts.

It goes without saying that platinum is practically never encountered in medicines except accidentally.

The filtrate from the platinum precipitate is evaporated to dryness in a tared porcelain crucible, ignited with a little oxalic acid, washed free from potassium chloride with water by decantation, again ignited and weighed as metallic gold. Or volumetrically, the gold in the form of neutral chloride free from all traces of nitric acid, is treated with a measured excess of tenth normal oxalic acid, allowed to stand until all of the gold is precipitated, and the excess of oxalic acid found by titrating with tenth normal solution of potassium permanganate; each cc. of oxalic solution consumed is equal to 0.00655 g. gold.

Qualitative Tests: Insoluble in all simple acids, soluble in nitro-hydrochloric acid, precipitated by ferrous sulphate, purple of Cassius precipitate by treating with stannous chloride containing a little stannic chloride.

The solution in the U-tube containing arsenic chloride along with some sulphur chloride, is boiled to expel free chlorine, hydrochloric acid added, and the arsenic again precipitated as arsenous sulphide as before.

The precipitate is washed with water, dried to con-
stant weight at 100° C., on a tared filter, and weighed;
61% of the weight of the precipitate is arsenic. Or
volumetrically, the precipitate is heated with 10 or
15 cc. of sulphuric acid, until the hydrogen sulphide,
and finally the sulphur dioxide are expelled, the acid
raised nearly to the boiling-point and the dark
color has disappeared. The solution is cooled, diluted
with water, nearly neutralized with sodium hydroxide,
made alkaline with sodium carbonate, and titrated with
tenth normal iodine, using starch indicator; each cc.
of the iodine solution consumed is equal to 0.0075 g.
of arsenic.

Qualitative Tests: Reinsch's test as already described
(page 32); Marsh's test, where the arsenic spots are
soluble instead of, as with antimony, insoluble in
sodium hypochlorite solution, brick red instead of,
as with antimony, white on drying with nitric acid,
and bright yellow instead of, as with antimony, orange
red, on drying with ammonium sulphide.

Gutzeit's Test: The arseniuretted hydrogen formed
from a small amount of the material in an evolution
flask containing arsenic, free hydrochloric acid, water
and zinc, after passing through a cotton plug in the
neck of the flask, will cause a distinct yellow stain on
a white filter paper cap placed over the flask and in the
center of which some alcoholic solution of mercuric
chloride has been dried. Ammonio cupric sulphate
gives with arsenous solutions a precipitate of Scheele's
green, while ammonio silver nitrate produces a bright
yellow precipitate in arsenous and a chocolate-colored
precipitate with arsenic solutions.

Sodium hydroxide and sodium carbonate produce
no precipitate.

The hydrochloric acid solution containing the antimony * and tin is treated with a few drops of nitric acid and boiled. Still keeping the solution near the boiling point, add pieces of pure bright iron wire as long as they dissolve and until the further addition of acid and iron produces no further precipitate of antimony. When all the iron is dissolved, add more hydrochloric acid, allow to settle, filter, wash with water containing more hydrochloric acid, and finally with alcohol and ether, dry at 100° C., on a tared filter and weigh as metallic antimony.

Or volumetrically the residue may be dissolved in considerable hydrochloric acid, sodium sulphite added in small portions, boiled until all of the sulphur dioxide is expelled, a drop of phenolphthalein added, then potash solution until red and again a slight excess of tartaric acid, and finally an excess of sodium bicarbonate, when the solution is immediately titrated with tenth normal iodine solution, each cc. of which is equivalent to 0.006 g. of antimony.

Qualitative Tests: Reinsch's and Marsh's tests as under arsenic. Strong solutions in hydrochloric acid are precipitated in the form of a basic salt by pouring into considerable water.

Sodium hydroxide and sodium carbonate precipitate as antimonic acid. Ammonio cupric sulphate and ammonio silver nitrate give no precipitates.

The acid solution containing iron and tin is treated with hydrogen sulphide in excess, allowed to stand some time, filtered, the precipitate washed with water containing a slight amount of hydrogen sulphide (if there

---

* Strong hydrochloric acid solutions of antimony may give a precipitate of basic salt on dilution with much water.

is a tendency for the precipitate to run through the filter use salt solution for washing and finally wash out the salt with ammonium acetate solution containing a little acetic acid). Dry the filter and precipitate, carefully incinerate the former, with a few drops of nitric acid, add and ignite the precipitate (covered) gently at first, then after removing the cover, more strongly until no odor of sulphur dioxide is noticeable, and finally heat strongly several times with the addition of pieces of pure ammonium carbonate until all of the sulphuric acid formed has been removed and the weight remains constant; 78.7% of the residue is tin.

Or Volumetrically: The precipitated sulphide is dissolved in hydrochloric acid, filtered, all hydrogen sulphide removed by boiling reduced by the gradual addition of pure iron wire, all of which must be dissolved, a fair quantity of Rochelle salt added together with an excess of sodium bicarbonate, and the mixture titrated with tenth normal iodine solution, each cc. of which is equal to 0.0059 g. of tin.

Qualitative Tests: Potassium or sodium hydroxide precipitates stannic salts as stannic acid, soluble in an excess of the precipitant. In the inner blowpipe flame the salts are reduced to metallic tin.

SEPARATION OF THE METALS OF GROUP FIVE

6. Heat the washed precipitate of the sulphides with nitric acid, add water, filter and add an excess of hydrochloric acid. After the precipitate of silver chloride, if any, has completely settled, the supernatant fluid is decanted through a filter, the precipitate again heated with strong nitric acid, diluted, filtered through the original filter, more hydrochloric acid added to the filtrate, heated for some time, filter again through

the second filter, and wash the second precipitate, consisting of silver chloride, if any, with water containing a little nitric acid, and determine the silver as in 1.

The above original precipitate of mercuric sulphide, which was insoluble in nitric acid, is washed quickly with water on a tared filter, dried at 100° C., washed with carbon disulphide to remove any separated sulphur if any, again dried, and weighed; 86.2% of the weight of the precipitate is mercury.

Or Volumetrically: Dissolve the sulphide in the water bath in nitro-hydrochloric acid, evaporate slowly to complete dryness, take up with a little water, and again evaporate completely to dryness until the neutral mercury bichloride results. Dissolve the latter in a definite measure of water, and add from a burette with constant stirring to a small definite measure of standard solution of potassium iodide (33.2 g. of pure salt to liter) until the first appearance of a permanent pink color from the mercuric iodide appears. Each cc. of the potassium iodide solution corresponds with 0.010 g. of mercury or with 0.0135 g. of mercuric chloride.

Qualitative Tests: Reinsch's tests as described above. Potassium iodide gives with mercurous salts pale yellow to green precipitates, with mercuric salts, cinnabar red precipitate soluble in excess. Stannous chloride reduces to metallic mercury, after heating.

Evaporate the filtrate from the silver chloride precipitate if any, to dryness, heat with nitric acid, add water and finally a good excess of sulphuric acid. Evaporate the fluid until the sulphuric acid begins to give off dense white fumes, allow to cool, add water and filter immediately from the insoluble lead sulphate,

wash the latter with water containing sulphuric acid, then with alcohol, and finally ignite, preferably in a Gooch crucible and weigh; 73.6% of the weight of the precipitate is lead oxide, and 68.3% is lead.

Or Volumetrically: Lead may be estimated by (a) treating an aliquot portion of the (acetic) solution with a measured excess of tenth normal oxalic acid, making up to a definite volume, allowing to stand some hours, removing an aliquot portion of the clear supernatant liquid and titrating with tenth normal potassium permanganate in the presence of sulphuric acid. Each cubic centimeter of oxalic acid combined with the lead to form oxalate equals 0.01032 g. of lead. Or (b) by proceeding similarly with tenth normal potassium dichromate, and later titrating the excess with tenth normal sodium thiosulphate; each cc. combined to form lead chromate is equal to 0.01032 g. of lead.

The filtrate and washings from the lead sulphate precipitate are evaporated and treated with an excess of ammonium hydroxide, which precipitates bismuth, but redissolves the hydroxides of copper and cadmium. To insure uniformity it is well to redissolve the bismuth precipitate if any in nitric acid, add water and a slight excess of ammonium carbonate solution, digest warm for some time, filter, wash and dry the precipitate. Remove the precipitate from the filter and ignite the latter gently with the addition of a few drops of nitric acid toward the end, then add the bulk of the precipitate and ignite carefully until the carbonic acid is all surely expelled and weigh. The bismuth trioxide weighed contains 89.65% of bismuth.

Or Volumetrically: The bismuth hydroxide may be dissolved in nitric acid, most of the excess of the latter evaporated, a considerable excess of oxalic acid solu-

tion added and the whole allowed to stand for some time until the precipitate has entirely settled. The supernatant fluid is decanted and the precipitate boiled several times with fresh portions of water until the reaction of the supernatant fluid ceases to be acid, when the bismuth will have been converted into the basic oxalate. A few cubic centimeters of sulphuric acid are then added to the solution, after which it is immediately titrated with decinormal potassium permanganate solution until a permanent pink color remains; each cc. of permaganate is equivalent to 0.0104 g. of bismuth.

Qualitative Tests: Bismuth and its salts are soluble in strong nitric or hydrochloric acid, from which solution an excess of water precipitates insoluble basic salts of the acid used.

The ammoniacal solution containing the copper and cadmium is acidified with hydrochloric acid, precipitated warm with hydrogen sulphide, the precipitated sulphides washed, and boiled with dilute sulphuric acid (1 to 5). This treatment dissolves the cadmium sulphide only. Wash the copper sulphide residue with water containing some hydrogen sulphide, dry quite rapidly, and after burning the filter add the precipitate to the crucible and ignite with some sublimed sulphur in a stream of hydrogen, or in hydrogen sulphide gas, and weigh; 79.85% of the precipitate is copper.

Or Volumetrically: The sulphide is digested with sulphuric acid, the excess driven off, the residue taken up with acetic acid and water, potassium iodide added, and the liberated iodine titrated with decinormal sodic thiosulphate solution; each cc. is equal to 0.0063 g. of copper.

Qualitative Tests: Ammonium hydroxide gives deep blue solutions of ammonio cupric compounds. Potassium ferrocyanide gives a red brown precipitate. Solutions deposit metallic copper on bright iron.

The filtrate from the copper sulphide precipitate, which may contain cadmium, is evaporated, ignited until all excess of sulphuric acid is removed, and weighed as cadmium sulphate; 54% of the residue is cadmium.

Or Volumetrically: It may be again precipitated and washed as sulphide, the filter and precipitate introduced into a large stoppered flask with 500 or 600 cc. of water, shaken until the precipitate is all finely divided, a moderate excess of hydrochloric acid added and titrated with decinormal solution of iodine; each cc. is equal to .0055 g. of cadmium.

Qualitative Tests: The yellow precipitate given with hydrogen sulphide from the acid solution is generally sufficient for identification.

METALS OF GROUPS THREE AND FOUR

7. Dissolve the ammonium sulphide precipitate in hydrochloric acid, boil with a few drops of nitric acid, cool, add water with a little ammonium chloride and then a slight excess of dry barium carbonate, and allow to stand for some time with occasional shaking. Decant the clear supernatant fluid through a filter and wash the precipitate with cold water. This precipitate contains the iron, aluminum and chromium, together with barium carbonate. The solution contains zinc, manganese, cobalt, nickel and barium salts. The precipitate is dissolved in the least possible quantity of hydrochloric acid, diluted with water and precipitated by boiling with a good excess of potassium hydroxide. The

precipitated ferric hydroxide is washed once by decantation, collected on a filter, and the washing completed with hot water containing a little ammonium hydroxide, the filter incinerated and the precipitate ignited in a tared porcelain crucible for weight, 70% of the ferric oxide weighed is iron.

Or Volumetrically: The precipitated ferric hydroxide is dissolved in hot dilute hydrochloric acid, a few pieces of pure zinc added to the solution, and the containing flask closed loosely with a well-greased cork until all of the zinc has dissolved, and the iron is completely reduced to the ferrous state. Decinormal potassium permanganate solution is now run in until the first permanent pink tint occurs. Each cc. so used corresponds with 0.0056 g. of iron.

Qualitative Reactions: Ferric salts, or ferrous salts after the addition of a drop of nitric acid or hydrogen dioxide, give a deep red color, and precipitate with ammonium or potassium sulfocyanide, and a deep blue one with potassium ferrocyanide.

To the filtrate containing the aluminum and chromium is now added about one-half the amount of potassium nitrate which was used of *actual* potassium hydroxide for precipitation, the solution evaporated preferably in a nickel dish and the dried residue fused thoroughly. Treat the fused mass with boiling water, supersaturate with hydrochloric acid, add a fair excess of potassium chlorate and evaporate to a syrupy consistency with further additions of potassium chlorate in quantities sufficient to remove all of the free hydrochloric acid. After diluting with water add an excess of ammonium carbonate and a little ammonium hydroxide, heat, filter, wash, dry and ignite the aluminum hydroxide; 53.04% of the weight is aluminum.

Or Volumetrically: The aluminum hydroxide is converted into sulphate, dissolved in water and the solution divided into two equal parts, to one part is added a neutral solution of Rochelle salt and then titrated with barium hydroxide, which gives the sulphuric acid existing free and combined with aluminum. The second portion is evaporated to dryness, taken up with neutral sodium citrate solution, and likewise titrated with barium hydroxide. The *difference* between the two amounts of barium hydroxide used is equivalent to one-third of the aluminum.

Qualitative Tests: Ammonium hydroxide gives a gelatinous precipitate insoluble in excess of the reagent. Potassium hydroxide gives a similar precipitate which dissolves in an excess.

To the filtrate, which now contains the chromium as chromic acid, is added a good excess of sodium acetate and acetic acid, and then neutral lead acetate until complete precipitation has occurred. Collect and wash on a tared filter, dry and weigh as lead chromate; 31.0% of the weight is chromic trioxide.

Or Volumetrically: The lead chromate is digested in a flask with water and a slight excess of sulphuric acid, and titrated with normal solution of ferrous ammonium sulphate until completer reduction has occurred, i.e., until the mixture has become green or until a drop of the fluid when removed to a white slab will just give a blue color with potassium ferricyanide; each cc. corresponds with .0517 g. chromium.

Qualitative Tests: Silver nitrate produces a purple red and lead acetate a canary-yellow precipitate in solutions of chromates, soluble in mineral acids.

The filtrate, which contains the zinc, manganese, cobalt, nickel and soluble barium salts, is treated with

a slight excess of sodium carbonate and without removing the precipitate from the flask, a slight excess of acetic acid added, hydrogen sulphide passed through the cold dilute solution and the resulting precipitate, if any, washed with water containing hydrogen sulphide and a little ammonium acetate. If the zinc sulphide is dark-colored it will generally indicate a contamination with cobalt or nickel due to too small an amount of acetic acid. Dry the precipitate, incinerate filter, and ignite the precipitate in a tared crucible in a stream of hydrogen gas; 67% of the weight is zinc.

Or Volumetrically: The precipitated sulphide after thorough washing until entirely free from hydrogen sulphide is placed with the filter in a flask, some water ferric chloride and hydrochloric acid added, the flask stoppered, and shaken for some time in a warm place until the supernatant fluid is of a yellow color and emits no odor of hydrogen sulphide. The flask is then nearly filled with cold water, more acid added if necessary, and decinormal potassium permanganate solution run in until a faint permanent pink color remains; each cc. so used represents 0.00327 g. of zinc.

Qualitative Tests: Ammonium sulphide gives a white precipitate soluble in hydrochloric acid. Ammonium hydroxide gives a gelatinous precipitate soluble in an excess of the reagent. All the zinc compounds with colorless acids are themselves colorless.

Evaporate the filtrate from the zinc sulphide precipitate, add an excess of sodium acetate and acetic acid, heat to 70° C., and again pass hydrogen sulphide, when the cobalt and nickel if any will be precipitated. Ignite the washed sulphides, dissolve in strong nitro-

hydrochloric acid by the aid of heat, dilute with water, filter, and boil the solution with an excess of sodium hydroxide; filter, wash the precipitate with hot water thoroughly, and ignite in a stream of hydrogen gas at first moderately and finally more strongly.

The cobalt or nickel or both are left in the metallic state, weigh and dissolve in nitric acid, neutralize with potassium hydroxide, add a solution of potassium or sodium nitrite and a slight excess of acetic acid and allow to stand in a warm place for twenty-four hours. Test a portion of the supernatant liquid for unprecipitated cobalt by again allowing it to stand with potassium or sodium nitrate and return this to the main solution if necessary, and finally, after being sure that the precipitation is complete, collect and wash the precipitated tripotassium cobaltic nitrite with a 10% potassium acetate solution containing a little potassium or sodium nitrite. Dissolve the precipitate in hydrochloric acid, heat nearly to boiling and add an excess of potassium hydroxide, after which continue the boiling until precipitate is of a brownish-black color. Collect the precipitate, wash thoroughly in hot water, ignite, wash again with hot water, and finally ignite in a stream of hydrogen as described above for weight as metallic cobalt. The difference between this and the weight of the two metals gives the nickel.

Qualitative Tests: Ammonium hydroxide gives a blue precipitate with cobalt and a green one with nickel, both soluble in an excess of the reagent.

In the filtrate from the cobalt and nickel sulphides, precipitate the manganese with yellow ammonium sulphide after adding an excess of ammonium hydroxide and some ammonium chloride. Allow the flask to stand some time and collect and wash the precipitate

with water containing a little ammonium sulphide and chloride. Incinerate the filter in a tared crucible, add the precipitate and some sublimed sulphur, and ignite in a stream of hydrogen for weight as manganous sulphide; 63.22% of the weight of the precipitate is manganese.

Or Volumetrically: Nearly boil the neutralized solution containing some sodium acetate and acetic acid with bromine water added as required until the manganese is all separated as manganese dioxide. Filter, wash, dissolve the precipitate in a measured quantity of decinormal solution of ferrous ammonium sulphate, which has been balanced against a corresponding decinormal solution of potassium permanganate, and finally titrate back with the decinormal permanganate until the first permanent pink color occurs. The difference between the permanganate solution so used and the amount which would have been used by the ferrous ammonium sulphate solution alone multiplied by 0.0055 gives the manganese.

Qualitative Tests: The formation of the flesh-colored precipitate soluble in acetic acid with ammonium sulphide is, in this place, quite conclusive. The precipitate from ammonium hydroxide with manganous salts is first white, becoming brown on standing and dissolves in oxalic acid with a rose color.

METALS OF GROUP TWO

8. Ignite the precipitate of alkaline earth * carbonates (or oxalates) in a tared crucible and weigh. If strontium or barium are to be determined dissolve the residue in nitric acid, evaporate to complete dryness, and

---

* Except magnesium.

digest with a quantity of equal parts of absolute alcohol and ether in a corked flask for some time, thoroughly breaking up the residue with a blunt glass rod. The calcium nitrate will dissolve and may be filtered and washed from the remaining nitrates of strontium and barium by the above mixture in a covered funnel. The liquid is evaporated from the calcium nitrate solution, and the residue ignited with sulphuric acid in a tared crucible for weight; 41.1% of the calcium sulphate is calcium oxide and 71.43% of the weight of this is calcium.

Or Volumetrically: The nitrate of calcium may be precipitated as oxalate by an excess of ammonium oxalate and a little ammonium hydroxide, allowed to stand in a warm place for some time, filtered, and the precipitate washed with water until perfectly free from the excess of ammonium oxalate, washed into a flask, some sulphuric acid added, and titrated with deci-normal permanganate until the first permanent pink color; each cc. so used corresponds with 0.0028 g. of calcium oxide or with 0.002 g. of calcium.

Qualitative Tests: Calcium gives a reddish-yellow flame and a characteristic spectrum. This and its precipitations with sulphates, and the precipitate with ammonium oxalate, which is soluble in hydrochloric acids, but not in acetic acid, will at this place satisfactorily identify the element.

The residue of barium and strontium nitrates is dissolved from the filter with a liberal amount of hot water, a few drops of acetic acid added, and then an excess of neutral ammonium chromate, after which the flask is allowed to stand for an hour or more. The precipitate is collected on a filter and washed with water containing a little ammonium chromate, and

finally with water alone until the color is all removed, after which the filter is incinerated and the precipitate ignited and weighed as barium chromate; 54.1% of the precipitate is barium.

Or Volumetrically: The nitrates are dissolved in considerable hot water and titrated with a solution of pure potassium dichromate (7.37 g. to liter) until on continuous shaking the yellow precipitate just ceases to form and the supernatant fluid has a very faint yellow color; each cc. is equal to 0.00684 g. of barium.

Qualitative Tests: Green flame coloration and characteristic spectrum, precipitation by a clear solution of calcium sulphate, and a pale yellow precipitate insoluble in acetic acid with potassium chromate.

The filtrate from the above is concentrated after the addition of a few drops of nitric acid, a slight excess of ammonium hydroxide and then ammonium carbonate added, and the resulting strontium carbonate washed onto a filter with water containing a few drops of ammonium carbonate solution. Ignite the precipitate with sulphuric acid in a tared crucible for weight as strontium sulphate; 56.4% of the weight of the precipitate is strontium oxide.

Or Volumetrically: Dissolve the well-washed carbonate in a measured excess of normal hydrochloric acid, and titrate back with normal solution of sodium hydroxide, using methyl orange as indicator; each cc. of acid consumed by the precipitate corresponds with 0.0438 g. of strontium.

Qualitative Tests: The intense red flame coloration and characteristic spectrum will sufficiently characterize strontium.

MAGNESIUM AND THE ALKALIES

9. Treat the ignited residue with a few drops of hydrochloric acid and dissolve in the least possible quantity of water. Add a considerable excess of a 25% solution of ammonium carbonate containing ammonium hydroxide and allow to stand for about twelve hours; filter off, wash with the same ammonium carbonate solution and finally once with water, returning the wash waters to the original filtrate, and ignite the precipitated ammonium magnesium carbonate strongly for weight in a tared crucible; 60.0% of the weight of the residual magnesium oxide is magnesium.

The above method, while more systematic, is not popular.

The following is more generally preferred. Dilute the hydrochloric solution to a definite measure. To one-half of this add ammonium chloride, ammonium hydroxide, and with constant stirring, sodium phosphate solution drop by drop. After standing for some time, preferably over night, the precipitated ammonium magnesium phosphate is collected, well washed with water containing ammonia, and strongly ignited; 21.88% of the precipitate is magnesium.

Or Volumetrically: The precipitated ammonio-magnesium phosphate is collected and well washed as before, and the ammoniacal water then washed out with 50% alcohol, after which the precipitate is dissolved off the filter with a measured amount of decinormal or normal hydrochloric acid, methyl orange added, and titrated back with a corresponding alkali; each cc. of decinormal acid consumed is equal to 0.0020% of magnesium oxide or to 0.0012% of magnesium.

Qualitative Tests: The precipitation with sodium

phosphate and the absence of flame coloration will characterize this element at this stage of the analysis.

If the ammonium carbonate method for separating magnesium has been followed, the filtrate is evaporated to dryness and cautiously ignited until all ammonium salts have been driven off. If, as is more generally the case, only one-half of the original solution has been used for the sodium phosphate precipitation, the remaining half is evaporated, ignited free from ammonium salts, again taken up and, if magnesium was found, evaporated with the addition of a little pure milk of lime toward the last, until the whole occupies but a few cubic centimeters. It is then filtered, the residue well washed ·with hot water, some ammonium hydroxide and ammonium oxalate added to the filtrate, allowed to stand until all of the added calcium is precipitated, again filtered and washed, evaporated to dryness and the ammonium salts again driven off by ignition. It is well to add a few drops of hydrochloric acid toward the last of the final evaporation to avoid spitting and to convert all of the remaining alkalies into chlorides. Extract the alkaline chloride residue with successive portions of a mixture of equal parts of absolute alcohol and ether, breaking up the residue with a blunt glass rod, and finally washing this residue with the ·same liquid. Withdraw a small portion of the alcohol-ether solution and apply the flame test for lithium. If the characteristic crimson flame and spectrum are obtained, evaporate the solution, gently ignite the residue with sulphuric acid, and weigh as lithium sulphate, 12.72% of this is lithium. This method always gives results which are too high as the lithium always contains traces of potassium, and hence the flame test and spectrum should always be

examined. The method of Gooch, using amyl alcohol, is more reliable but hardly necessary for drug work.

Or Volumetrically: The residual lithium chloride, instead of being ignited and weighed as sulphate, may be dissolved in water, a few drops of potassium chromate added, and titrated with decinormal silver nitrate solution until the first permanent reddish color; each cc. so used is equal to 0.0042 g. lithium chloride or to 0.007 g. lithium.

Qualitative Tests: The solubility of the chloride in ether-alcohol, and the characteristic crimson flame coloration and spectrum are amply sufficient.,

The residue of potassium and sodium chlorides is dissolved in a tared porcelain dish in a small quantity of water and treated with a few drops of hydrochloric acid and sufficient platinic chloride solution to maintain a decided yellow color in the solution. The concentration should be such that no permanent precipitate will remain when the mixture is warmed on the water bath; if so, add more water. It is then evaporated until a crust begins to form, and treated with 80% alcohol, filtered, and the residue, if any, washed with 80% alcohol. Finally any slight precipitate on the filter is washed back into the dish with hot water, and the whole evaporated, dried, and weighed as potassium platinic chloride; 16.11% of this weight is potassium.

Qualitative Tests: The formation of the platinum double salt as above and the characteristic flame coloration and spectrum are sufficient.

From the filtrate from the above, the platinum is precipitated by hydrogen sulphide, and together with the potassium platinic chloride saved for recovery of the platinum. The filtrate is then evaporated, gently

ignited, and weighed as sodium chloride; 39.38% of the weight is sodium.

Qualitative Tests: The strong yellow flame coloration and spectrum are sufficient.

Volumetrically: Both the potassium platinic chloride and the sodium chloride may be determined by titration with decinormal silver nitrate solution, using sufficient warm water for the solution of the platinum double salt. In these cases each cc. of silver solution is equal to .0013 g. of potassium and 0.0023 g. of sodium respectively.

SEPARATION AND DETERMINATION OF ACIDS

The acids unfortunately do not admit of being separated into as well-defined groups by reagents as do the bases, and the systematic separation of the members of these various groups is still less satisfactory, and where the amount of material is sufficiently large, it is generally well to use separate portions for the various determinations.

On the other hand, as the number of mineral acids occurring in most medicinal mixtures is generally small, and as the analyst has already accurately determined the various bases with which these acids are as a rule all combined, in definite proportions, it is seldom necessary to determine the latter as accurately as we would the various metals, as the quantities of these latter furnish the measure of the acids which would necessarily have been combined with them, in fact a qualitative analysis with an approximate idea of the relative quantities of acids only is often sufficient. For example, in a clear mixture containing only a considerable known quantity of potassium and but

little mercury, along with considerable iodine and but little chlorine, it is fair to assume that potassium iodide and mercuric chloride were the materials originally introduced, without knowing the exact quantities of the two halogens.

In following the scheme below it will often be possible for the analyst to omit entire steps in the operation as the previous reactions or treatment of the material will assure him of the absence of many acids. Arsenic, chromium, manganese, etc., in the form of their higher oxides, in combination with bases as arseniates or arsenites, chromates, dichromates, permanganates, etc., will of course have been separated and determined along with the metals, as their solutions are reduced and precipitated with separation of sulphur by continued treatment with hydrogen sulphide or ammonium sulphide, while hydrosulphuric, carbonic, sulphurous, hydrocyanic, hypochlorous, thiosulphuric, etc., will have been detected by effervescence or their characteristic odor on first acidifying and warming the original solution preparatory to separating the metals, except where they have been decomposed or expelled by previous treatment of the mixture with oxidizing agents.

Many organic acids, especially the fatty acids and those derived from the benzene series of hydrocarbons, e.g., salicylic, benzoic, etc., are precipitated or liberated as insoluble floating masses by this original acidification and may be "shaken out" in a separator by an appropriate solvent, usually petroleum ether, before proceeding further. In aqueous residues from a previous extraction by immiscible solvents, these acids will, of course, be absent, as they will also be in ash residues or after destroying organic matter by

oxidation in the wet way. The organic acid salts of the alkalies and alkaline earths are decomposed by ignition, leaving the fixed bases in the form of carbonates, or as in the case of certain of the heavy metals, as oxides, so if an acid or neutral mixture on drying and igniting leaves an alkaline residue evolving carbonic acid gas on treatment with an acid, and especially if during the ignition it separates carbon, it furnishes proof of the presence of some organic acid; but nitrates, etc., when ignited with carbon or what amounts to the same thing with organic materials, also are changed to carbonates. The deflagration which ensues in these cases is, however, generally sufficient evidence of the nature of the substance. The following is a tentative, although in most cases not quantitatively accurate scheme for separating the acids. The reactions described would be often interfered with were all of the acids to occur in the same solution (in this case some would decompose others), but as this is almost an imaginary condition no further comment is made, both for the sake of simplicity and for the reasons before stated.

MINERAL AND COMMON ORGANIC ACIDS

1. If not already in solution, dissolve in water, or if still not entirely soluble, after dilution and persistent heating, filter off the water-soluble portion and dissolve the residue in nitric acid and water and examine each separately. In the examination of the nitric acid solution considerable care must be exercised to correctly interpret the results of the action of the acid. If the reaction is acid, in which case carbonic acid will probably have escaped and silicic acid, if present,

will be separated as a flocculent or gelatinous pre-
cipitate.   Neutralize with barium hydroxide (1), ADD AN
EXCESS OF BARIUM NITRATE, heat and allow to stand
until settled clear.   Precipitated are the barium salts
of sulphuric, sulphurous, phosphoric, phosphorous,
carbonic, boric, arsenic, chromic, hydrofluoric, oxalic,
tartaric, citric, salicylic, benzoic and fatty acids.
Examine precipitate by 2.

2*a*. Transfer the slightly washed precipitate from
the above to a round-bottomed evolution flask and treat
slowly with slight excess of hydrochloric acid and sweep
out all of the gaseous contents with an air current.
Evolved is carbonic acid,* which should be passed into
a suitable absorption apparatus, bulbed U-tubes or
Mayer's bulbed tube, holding a clear solution of barium
hydroxide.   Filter off the precipitated barium car-
bonate, wash with recently boiled water, incinerate
filter in a tared crucible, add the precipitate, ignite
gently, and weigh; 22.33% of the barium carbonate
found is carbon dioxide.

Or Volumetrically: Dissolve the washed precipitate in a
measured excess of standard normal acid, adding the filter
to the flask, and titrate back with normal alkali, using
methyl orange as indicator; each cubic centimeter of
acid consumed is equal to 0.022 g. of carbon dioxide.

b. Shake out the residual acid liquid in the evolu-
tion flask with successive portions of petroleum ether
or benzene, evaporate the united separates to dryness
in a tared dish in an air current, allow to stand in a
desiccator for some time and weigh.   Removed may be
salicylic, benzoic and possibly other aromatic acids, and
perhaps fatty acids.   Should the last-named be present,
as evidenced by the oily nature of the residue, dissolve

---

* Possibly also sulphurous acid.

out the aromatic acids by digesting with 25% alcohol and allow this solution to evaporate in another dish, weigh the original dish after drying again, and calculate the aromatic acids from the loss. Determine the melting point of these, and if it is not regular, recrystallize until one or more pure acids are obtained, well crytallized and with their normal melting point; also, dissolve them in just sufficient weak soda solution to make a *neutral* solution, and add a little *neutral* ferric chloride solution. *Benzoic acid* under these circumstances gives a flesh-colored and *salicylic acid* a violet-colored reaction product. The melting point of benzoic acid is 122° C., and of salicylic acid 156° C. For the melting points and other characters of the fatty acids consult Table 6.

c. Distill the acid residue from the petroleum ether extraction in streaming steam until the distillate is free from sulphurous acidity, and titrate with tenth normal iodine solutions, in case the distillate reacts for sulphurous acid, each cc. of which is equivalent to 0.0032 g. of *sulphur dioxide*. To the residue in the flask add methyl alcohol and distill in a current of methyl alcohol delivered to the bottom of the distilling flask from a second boiling flask, until the distillate is no longer acid, add 30% by volume of glycerin, a few drops of phenolphthalein and titrate with normal soda solution, one cc. of which is equivalent to 0.062 g. of *boric acid* (H_3BO_3).

d. Filter and wash the insoluble precipitate, which will probably consist of barium combined with the *sulphuric acid* as barium sulphate, although it may also consist of barium *fluoride* or of *silicic acid*. Fluorides are at present practically unknown in medicine and silicic acid if present in small amounts is almost cer-

tainly accidental. The precipitate of barium sulphate is accordingly ignited, and weighed after a second ignition after the addition of a few drops of nitric acid; 34.33% of the weight of the barium sulphate precipitate is sulphur trioxide.

To insure against mistakes here, it is well after this last weighing to treat the precipitate with repeated portions of hydrofluoric acid.

e. Neutralize the filtrate from the above barium sulphate precipitate with ammonium hydroxide, and add a slight excess. To the liquid an excess of acetic acid is now added, the whole allowed to stand and filtered. The *insoluble residue* may consist of *oxalic,* *tartaric*, or if colored *chromic* or *manganic acids*, etc. In the latter cases the elements will probably have already been determined along with the metals. The precipitate is suspended in water, dissolved in the least possible excess of hydrochloric acid, and carefully decomposed by adding saturated solution of potassium sulphate until no further precipitate of barium sulphate is formed after heating, and after settling clear, filtered. The filtrate is made up to a definite volume, and polarized for tartaric acid.

An aliquot portion is also treated with sulphuric acid and titrated with tenth normal solution of potassium permanganate, each cc. of which is equivalent to 0.0063 g. of oxalic acid. The solutions are again mixed, neutralized, evaporated to dryness, ignited, and the residue dissolved in water, filtered if necessary, and treated with lead acetate. The washed lead chromate precipitate is dried, ignited and weighed; 31.00% is *chromium trioxide*.

Or Volumetrically: The lead chromate is introduced into a bottle having an accurately ground stopper,

and into which some saturated solution of potassium iodide and hydrochloric acid have been placed, the stopper clamped in and the tightly closed bottle heated in a water bath to boiling, cooled, and the liberated iodine titrated with tenth normal sodium thiosulphate. One part of the iodine so found is equivalent to 0.3346 parts of *chrominm trioxide.* In place of the digestion in the closed bottle, the chromate may be distilled with hydrochloric acid and the liberated chlorine conducted into the iodide solution contained in a bulbed tube.

f. The filtrate from the above, soluble in acetic acid, may contain *phosphoric, phosphorous, arsenic, arsenous,* or *citric, acid.* The arsenic of arsenic acids will have been previously determined with the metals, and if present may now be removed by hydrogen sulphide with addition of hydrochloric acid. The liquid is evaporated to dryness, gently ignited, and the water solution of the residue titrated with tenth normal acid, each cc. of which is equivalent to 0.0070 *citric acid.* The residue is again extracted with dilute hydrochloric acid and water, rendered alkaline with ammonium chloride and ammonia, precipitated cold with magnesia mixture added slowly drop by drop with continuous stirring, and after standing for some hours the precipitate is collected, washed with water containing ammonia, strongly ignited and weighed; 65.0% of the weight is *phosphoric oxide* (P_2O_5).

Or Volumetrically: The precipitate is washed free from ammonia with dilute alcohol, dissolved in a measured excess of tenth normal acid, and titrated back with tenth normal soda. Each cc. of tenth normal acid is equal to 0.0035 g. of phosphoric oxide or to 0.0075 g. of arsenous oxide, As_2O_3, which must be allowed for in case arsenic is also found.

2. Acidify the filtrate from 1 with nitric acid (silicic acid may precipitate and carbonic acid may escape) AND ADD AN EXCESS OF SILVER NITRATE. Precipitated are *hydrochloric, hydrobromic, hydriodic, hydrocyanic,* and *sulphocyanic* acids. After neutralizing with ammonia *arsenous* acid will also be precipitated as will also traces of citric, tartaric, salicylic acid, etc., which were not precipitated by barium.

a. Dry the washed precipitate at 100° C. and weigh. Digest an aliquot portion in nitric acid, specific gravity 1.20, at 150° C. for one hour or at 100° C. for several hours, dilute with water, filter and wash the halogen precipitate free from any silver salts of sulphocyanic, cyanic, hydrocyanic, or hydrosulphuric acids, which may have been found, dry it at 100° C., and weigh. The halogen silver salts may generally be separated sufficiently well for our present purpose by digesting the weighed precipitate with a measured amount of ammonium hydroxide solution, specific gravity 0.960, filtering off and washing the insoluble silver iodide, and separating the silver bromide and chloride in the filtrate. One milligramme correction must be added for each 2.5 cc. of ammonia used, as representing the solubility of silver iodide in that liquid. The silver chloride and bromide are precipitated by adding a slight excess of nitric acid, collected, transferred to a tared bulb tube of hard glass, dried (fused) and weighed. The bulb containing the silver salts is then heated over a small flame until the salts are fused and a slow stream of chlorine allowed to pass through, and this in turn swept out by air and the tube cooled. The loss of weight multiplied by 4.223 is equal to the silver *bromide,* 42.55% of which is *bromine.* The difference between this and the original weight of the two halides soluble

in ammonia is of course the silver chloride, 24.73% of which is *chlorine*.

b. Heat the nitric acid filtrate from the silver halides and precipitate with an excess of barium nitrate, ignite, weigh, and from the amount of sulphur in the barium sulphate found, calculate the amount of sulphocyanic, cyanic acids or of hydrogen sulphide which would correspond with this. Hydrocyanic acid is when necessary estimated directly in the reserved portion of the original silver nitrate precipitate, or may be calculated from the loss of weight of the precipitate in *a* plus the calculated weight of any silver salt of a sulphur acid which may have been present, if any. The *arsenous acid* will probably have been determined with the metals or as arsenic acid (formed from the arsenous acid originally present by oxidation). If not it may now be measured by either of those methods.

3. *In the filtrate* from 2 are *acetic*, *nitrous*, *chloric*, *hypochlorous*, *formic*, and the added *nitric acid*, together with any nitric acid originally present. When chloric, nitrous, nitric, or rarely hypochlorous acids are also present, the filtrate is treated with strong potassium iodide and hydrochloric acid, digested as in *e*, under the determination of chromic acid, and the liberated iodine titrated with tenth normal sodium thiosulphate from the volume of which the chloric acid, combined always as chlorates, may be calculated. If hypochlorites are present, they may be determined in similar manner directly without digestion by adding some acetic acid along with the potassium iodide. One cc. in each of these cases equals 0.003550 g. chlorine. The mixture is then transferred to a flask, zinc granules, iron and an excess of strong potassium hydroxide added, and slowly distilled into a measured excess of normal

or tenth normal acid, until all of the ammonia formed from the nitric acid is evolved, and the remaining acid determined by titration. Each cc. of acid so killed is equal to 0.0540 g. of *nitric pentoxide* (N_2O_5). It is generally advisable to introduce a safety tube during the distillation to prevent traces of fixed alkali being carried over. When nitrites are also present they are generally in small amounts only and are best estimated in a manner similar to the one used in water analysis. A small portion of the original neutral white solution is treated with from one-half to one cc. of a three-tenths per cent solution of sulphanilic acid in 30% acetic acid, and a like amount of 0.05% α-naphthylamine solution, also in 30% actual acetic acid. After five minutes the scarlet color produced is measured by matching it against the color of a solution containing a known amount of pure sodium nitrite which has been in every way similarly treated. Very small amounts of nitrous acid have many times been entirely changed to nitric acid by the oxidizing processes of the various operations previously described, and due allowance must accordingly be made for this possibility and extra precautions taken to avoid confusion.

The residue in the flask remaining after distilling off the ammonia from the nitric acid is treated with a fair excess of sulphuric acid and distilled (conveniently with live steam) until the distillate is free from acidity, and the latter titrated with normal or tenth normal carbonated alkali for *acetic acid*, each cc. of which is equal to 0.00598 g.

Where formic acid is present, as is rarely the case, an excess of the sodium carbonate solution is added together with a measured *excess* of normal or tenth

normal solution of potassium permanganate, and the solution warmed. The liquid is next acidified with sulphuric acid, a measured excess of normal or tenth normal oxalic acid added, until the manganese hydroxide previously formed is redissolved and the permanganate just decolorized. The excess of oxalic acid is then titrated with tenth normal potassium permanganate, each cc. of which used to oxidize the *formic acid*, as determined by the difference between the total volume of solution used and that used to oxidize the oxalic acid, is equivalent to 0.0046 g. of *formic acid*.

QUALITATIVE TESTS FOR COMMON ACIDS.

Carbonic. Precipitates calcium and barium hydroxide solutions and is liberated from its combinations by all other acids; precipitates with soluble salts of most of the heavy metals.

Boric. Moistened with hydrochloric acid it still colors turmeric paper brown, after drying. Gives a chracteristic green flame and spectrum; precipitates calcium, barium and silver salts.

Silicic. Insoluble in all acids, gives a characteristic so-called "silica skeleton" in a bead of miscrocosmic salt. Volatilized by igniting with hydrofluoric and sulphuric acid, but not by direct ignition.

Sulphuric Acid. Precipitate with barium chloride insoluble in all acids. Precipitate with soluble lead salts soluble in concentrated acids, and ammonium acetate. Heated with sodium carbonate on charcoal, hepar is formed which gives a brown or black stain on silver with dilute acids.

Sulphurous Acid. Decolorizes acid solutions of potassium permanganate, and gives green color with potas-

sium dichromate.   Characteristic odor of sulphur dioxide when treated with sulphuric acid.

Phosphoric Acid.   Gives a white precipitate soluble in acids with a mixture of ammonium chloride, magnesium sulphate and ammonia.   Ammonium molybdate gives a yellow precipitate insoluble in nitric acid, soluble in ammonia.

Hydrochloric Acid.   Silver nitrate gives a white curdy precipitate soluble in ammonium hydroxide, insoluble in nitric acid.   Lead acetate gives white precipitate soluble in hot water.

Hydrobromic Acid.   Silver nitrate gives a slightly yellowish white precipitate sparingly soluble in ammonium hydroxide, insoluble in acids.   Chlorine liberates bromine from water solutions of bromides, which former may be shaken out with chloroform and colors starch yellow.

Hydriodic Acid.   Silver nitrate gives a pale yellow precipitate, practically insoluble in ammonium hydroxide; lead acetate gives a precipitate of yellow lead iodide; chlorine liberates iodine from iodides, which may be shaken out with chloroform and colors starch blue.

Chromic (dichromic), manganic, and permanganic acids. These are reduced by hydrogen sulphide and then give precipitates which react like those described under the corresponding metallic bodies.

Arsenic Acid.   Gives a yellow precipitate after passing hydrogen sulphide for some time, which reacts for arsenic generally; gives a white crystalline precipitate soluble in acids with magnesia mixture, and in other respects reacts similarly to phosphoric acid.

Arsenous Acid.   Gives yellow precipitate of arsenous sulphide with hydrogen sulphide and otherwise reacts as under metallic arsenic.

Hydrofluoric Acid.   Evolved by warming gently with sulphuric acid it etches glass.

Hypophosphorous Acid.   Neutral salts burn with phosphorescence, and precipitate metallic mercury and silver from solutions of their salts.

Hydrosulphuric Acid (hydrogen sulphide).   Sulphur odor; blackens and precipitates lead, copper or iron salts, etc.

Nitric Acid.   Heated with copper turnings evolves red fumes, the same occurring with nitrates after acidifying strongly with sulphuric acid.   It decolorizes indigo and deflagrates when its salts are heated on charcoal.

Nitrous Acid.   Gives characteristic red color even in very dilute solutions when mixed with a few drops of 0.3% solution of sulphanilic acid and a like amount of 0.05% solution of *a* naphthylamine, both in 30% acetic acid.

Chloric Acid.   Exists only as salts, which deflagrate on charcoal, and liberate iodine from potassium iodide after adding hydrochloric acid.

Thiosulphuric Acid.   Sulphur dioxide and sulphur on adding hydrochloric acid.

Hypochlorous Acid.   Has a chlorinous odor and liberates iodine from potassium iodide directly.

ORGANIC ACIDS

Acetic Acid.   Warmed with alcohol and sulphuric acid a fragrant odor of acetic ether is evolved.   Neutral salts give a deep red color with ferric chloride, which yields a bulky red precipitate on boiling.   Volatile with steam.

Oxalic Acid.   Alkaline salts do not blacken when ignited; evolve carbon monoxide and dioxide when

heated with strong sulphuric acid; give precipitate with calcium chloride; insoluble in acetic acid, soluble in hydrochloric acid.

Citric Acid. When boiled with calcium chloride solution gives a precipitate *insoluble* in potassium hydroxide. Silver nitrate gives a white precipitate which does not blacken on heating. Solutions do not decolorize acid potassium permanganate.

Tartaric Acid. When boiled with calcium chloride solution gives a precipitate *soluble* in potassium hydroxide solution. Silver nitrate gives a white precipitate which blackens on heating. Decolorizes acid potassium permanganate solution.

Hydrocyanic Acid. Silver nitrate gives a white precipitate sparingly soluble in ammonium hydroxide, insoluble in nitric acid, with ammonium sulphydrate; it gives ammonium sulphocyanide, which latter gives an intense blood-red color with ferric salts. Treated with a small amount of a ferrous and of a ferric salt; a slight excess of potassium hydroxide solution gives a greenish precipitate, which latter on being dissolved in hydrochloric acid gives a precipitate of Prussian blue.

Sulphocyanic Acid. The deep blood-red color given with ferric salts is sufficiently characteristic.

Formic Acid. The acid and its salts reduce gold, silver, and mercury solutions on boiling and yield deposits of the metals. Free acid volatile with steam.

Fatty Acids. Oily, insoluble in water, crystallize on cooling, unite with sodium or potassium hydroxide solution to form soaps which lather freely. See tables for melting-points, etc.

Salicylic Acid. White crystals, practically insoluble in water; solutions of salts of free acid give a deep violet color with ferric chloride. Melting-point 117° C.

Benzoic Acid. White crystals practically insoluble in water; salts give a flesh-colored precipitate with ferric chloride; sublimes easily, melting point 120° C.

The qualitative separation and identification of common inorganic materials is more quickly presented in the following tables:

QUALITATIVE ANALYSIS OF INORGANIC MEDICINES

1. SEPARATION OF METALS INTO GROUPS

HYDRO-CHLORIC ACID PRECIPITATES	HYDROGEN SULPHIDE PRECIPITATES		AMMONIUM SULPHIDE AND HYDROXIDE PRECIPI-TATES	AMMONIUM CARBONATE PRECIPI-TATES	LEFT IN SOLUTION ARE
	Insoluble in (NH₄)₂S.	Soluble in (NH₄)₂S.			
Fifth Group.		*Sixth Group.*	*Third and Fourth Group.*	*Second Group.*	*First Group.*
(*white*) AgCl Hg₂Cl₂ PbCl₂	(*black*) PbS HgS Bi₂S₃ CuS (*yellow*) CdS	(*yellow*) As₂S₃ Sb₂S₃ SnS₂ (*brown*) SnS Au₂S₃ PtS₂	(*black*) FeS CoS NiS (*yellow*) MnS (*green*) Cr₂(OH)₆ (*white*) Al₂(OH)₆ ZnS	(*white*) CaCO₃ BaCO₃ SrCO₃	(*white*) Mg K Na Li

2. PRECIPITATED BY HYDROCHLORIC ACID

GROUP 5, DIVISION I

Boil with *considerable water* and filter hot.

FILTRATE.	DIGEST RESIDUE WITH AMMONIUM HYDROXIDE.	
PbCl₂. Add sulphuric acid or sulphate. (White ppt.) PbSO₄.	**Solution.** AgCl(NH)₄Cl. Add nitric acid, precipitate of AgCl.	**Residue.** (NH₄)HgCl from Hg₂Cl₂.

3. PRECIPITATED BY HYDROGEN SULPHIDE AND *INSOLUBLE* IN AMMONIUM SULPHIDE
GROUP 5, DIVISION II

Heat with nitric acid and filter.

RESIDUE.	FILTRATE.		
$HgS.$ Soluble in nitro-hydrochloric acid, red HgI_2 with potassium iodide. $PbSO_4$. White powder soluble in ammonium tartrate. *S.* Yellow combustible, soluble, in carbon disulphide.	*Add sulphuric acid.*		
	Precipitate. $PbSO_4$. White powder soluble in ammonium tartrate.	**Solution.** *Add excess of ammonium hydroxide.*	
		Precipitate. $Bi(OH)_3$. Dissolve in HCl and add to water. BiOCl.	**Filtrate.** *Divide into two parts.* *Cu.* Red precipitate with potassium ferrocyanide. *Cd.* Add KCN and H_2S, yellow precipitate.

4. PRECIPITATED BY HYDROGEN SULPHIDE AND *SOLUBLE* IN AMMONIUM SULPHIDE
GROUP 6

Boil with strong hydrochloric acid.

RESIDUE.	SOLUTION.		
As_2S_3. Dissolve in HCl and $KClO_3$ and examine by Marsh's test. Au_2S_3 and PtS_2. Special tests.	Add a few drops of nitric acid and boil. While still hot saturate with iron wire.		
	Precipitate. *Sb.*	**Solution.** Add excess of nitric acid, evaporate to dryness, and redissolve in water.	
		RESIDUE. SnO_4.	SOLUTION. Added iron.

5. PRECIPITATED BY AMMONIUM SULPHIDE AND AMMONIUM HYDROXIDE—GROUPS 3 AND 4

Dissolve in warm dilute hydrochloric acid, add a few drops of nitric acid, ammonium chloride, and finally an excess of ammonium hydroxide and *boil.*

Precipitate.		Filtrate.	
Dissolve in hydrochloric acid and add excess of potassium hydroxide.		Add acetic acid in excess and pass hydrogen sulphide gas.	
Precipitate.	FILTRATE.	PRECIPITATE.	FILTRATE.
$Fe(OH)_2$. Dissolve in dilute hydrochloric acid and add potassium ferrocyanide. Blue ppt.	Add excess of hydrochloric acid, and then excess of ammonium carbonate. $Al(OH)_3$ (*white*). Boil the solution for some time. $Cr(OH)_3$ (*green*).	ZnS (*white*), CoS (*black*), NiS (*black*).	Add ammonium hydroxide and ammonium sulphide. MnS (*yellow*).

6. PRECIPITATED BY AMMONIUM CARBONATE
Group 2

Dissolve in acetic acid and add potassic chromate.

Precipitate.	Filtrate.	
$BaCrO_4$ (*pale yellow*).	Add very dilute sulphuric acid and allow to stand.	
	PRECIPITATE. $SrSO_4$ (*white*).	FILTRATE. Add excess of ammonium hydroxide and then ammonium oxalate. CaC_2O_4 (*white*).

7. LEFT IN SOLUTION—Group 1

Divide solution into two parts. To one part add sodium phosphate, a white crystalline precipitate, indicated *Mg*. Evaporate the other portion to dryness, ignite, until ammonium salts are driven off and test by flame colorations for *Na*, *K*, and *Li*.

QUALITATIVE REACTIONS OF COMMON ACIDS
(Precipitates)

Barium Chloride.	Calcium Chloride.	Magnesia Mixture.	Ferric Chloride.	Silver Nitrate with HNO$_3$.
† Acids.	† Acids.	† Acids.	† Acids.	—
Sulphuric	Sulphuric	—	—	—
Sulphurous	Sulphurous	—	—	—*
Phosphoric	Phosphoric	Phosphoric	Phosphoric	—*
Phosphorous	—	—	—	—*
Carbonic	Carbonic	—	FeCO$_3$	—*
Boric	Boric	—	Boric	—*
Arsenic	Arsenic	Arsenic	Arsenic	—*
Arsenous	—	—	—	—*
Chromic	—	—	—	—*
Oxalic	Oxalic	—	Oxalic	—*
Tartaric	Tartaric	Tartaric	—	—*
Citric	Citric	—	—	—
—	—	—	Ferrocyanic	Ferrocyanic acid
—	—	—	Sulphocyanic	Suplhocyanic acid
—	—	—	Acetic (red color)	—
—	—	—	Hydrogen sulphide	Hydrogen sulphide
—	—	—	—	Hydrochloric
—	—	—	—	Hydrobromic
—	—	—	—	Hydriodic
—	—	—	—	Hydrocyanic

* Silver nitrate gives precipitates with these acids in *neutral* solutions.
† These precipitates are all soluble in hydrochloric acid and most other mineral acids, except barium sulphate.

CHAPTER IV

ULTIMATE ORGANIC ANALYSIS

ULTIMATE or elementary analysis is frequently required for the purpose of fixing the identity of organic bodies separated from medicinal mixtures. Where these bodies are at all well known and their composition and properties already determined and recorded, as is generally the case, they may as a rule, however, be more quickly and equally as accurately identified by their crystalline form, specific gravity, melting-point, boiling-point, precipitation and color reactions, solubility and decomposition products, and occasionally also by their refractive index, rotation of the plane of polarized light, or electric-conductivity. Of all these physical properties the first four are most easily determined and furnish the information which is most generally sought. The amount of material which is available for analysis is also often too small to allow of separating a sufficient quantity of some of the ingredients, to allow of a combustion being made. In other cases, however, an elementary analysis may be very desirable as a check on the other reactions, and in the study of the compounds which may possibly be separated from new or poorly studied sources it becomes almost a necessity.

All organic bodies contain carbon and hydrogen, and most medicinally active ones contain, in addition to these, oxygen and frequently nitrogen, besides

often sulphur, phosphorus, the halogens, and the metals, although it is of course possible that any element may occur combined in them.

The determinations of these elements in organic combination have since the time of Lavoisier (1780) been made by the complete combustion of the substance by the aid of suitable oxidizing material and the quantities of the several elements calculated from the data obtained by collecting and measuring the products of this combustion, essentially as is done at the present time, and while numerous improvements in the apparatus and methods are made from time to time, it seems highly unlikely that any marked departure from these original principles will be made.

There are required for the work as described below a suitable combustion furnace for heating tubes, of which Fig. 12 shows a common type; combustion tubes of hard glass or porcelain of from twelve to fifteen millimeters in diameter and generally about one meter long; calcium chloride tubes and Geissler potash bulbs, the latter connected again to a small tube to contain solid potassium hydroxide; wash bottles and calcium chloride towers for purifying air and oxygen gas; a platinum, porcelain or copper boat or trough which will slip loosely inside the combustion tube; either some practical form of aspirator or gas delivery apparatus, and the following reagents:

Oxygen gas; granular copper oxide; granular metallic copper or copper foil, reduced by being successively ignited and plunged hot into methyl alcohol and dried; strong potash solution; dry granular calcium chloride; potash and soda-lime and sodium peroxide free from chlorine sulphur and phosphorus, or at least containing accurately known quantities of these.

Of late, attempts have been made at determining the elementary composition of organic bodies by measuring the products resulting from their combustion in oxygen gas under high pressure in a closed bomb calorimeter after the method of Berthelot, used in determining the heats of combustion of carbon compounds. Carbon, sulphur, nitrogen and phosphorus seem capable of being determined with fair accuracy, but a satisfactory method for measuring the water formed from the combustion of the hydrogen seems not yet to have been arrived at. The apparatus needs to be very strongly built, lined with a non-corrosive lining like gold or platinum, and is very expensive; but when already at hand for the purpose for which it was made, the last objection of course does not prevail. The oxygen is used under a pressure of from twenty-five to forty atmospheres, and must be free from the elements which are to be determined.

Success in elementary organic analysis depends on a close application to details, and when possible analyses should be repeated a number of times and the average taken. When beginning with new apparatus or methods it is well for the analyst to work with pure substances of known composition, e.g., cane sugar, acetanilide, etc., until continued constant results are obtained, before attempting to make a combustion of the substance under examination.

Qualitative Tests

Carbon and Hydrogen are necessarily present if the substance under examination is known to be an organic compound, if not, the blackening which generally results from the carbonization of the body on porcelain or platinum foil is sufficient indication of carbon,

when it occurs, but a safer and altogether more satis-
factory method consists in heating a small amount
of the substance with cupric oxide in a glass tube,
the substance, oxide and tube being throughout dry,
when the carbon will be burned to carbon dioxide,
which will give a precipitate of barium carbonate
when passed through clear barium hydroxide solu-
tion, and the hydrogen burned to water, which will
condense in the cooler parts of the glass tube, and will
produce a blue color in paper impregnated with thor-
oughly dry copper sulphate or chloride.

Nitrogen may be detected by the odor of burning
hair when the substance is burned, but more accurately
by heating the substance in a tube with lime or soda-
lime, when the nitrogen will be evolved as ammonia,
which will blue moistened red litmus paper held
at the mouth of the tube. A more sensitive method
which may be desirable in some cases consists in heat-
ing the substance with dry metallic sodium, dissolving
in water, adding a drop or two of solution of ferrous
sulphate, an excess of hydrochloric acid, and finally
one or two drops of ferric chloride solution when, in
the presence of any organic nitrogen, a precipitate
of Prussian blue will be formed.

Sulphur, Phosphorus, Chlorine, Bromine, and Iodine
may all be detected by mixing a small amount of the
substance with about ten times its weight of sodium
peroxide, known to be free from these elements, heat-
ing in a small metal tube or crucible until deflagration
ensues, dissolving out the fused mass with distilled
water, acidifying with nitric acid, boiling to expel
all loosely combined oxygen, and testing aliquot por-
tions for sulphuric acid with barium chloride, phos-
phoric acid with ammonium molybdate or magnesia

mixture and the halogens with silver nitrate. In some instances modifications of this simple method will be desirable and must be met as circumstances require.

Metals. and Other Non-metallic Elements than those already mentioned which may be present may be detected after the manner described in the preceding chapter, either by ashing the substance, or, what is preferable, destroying the organic matters by oxidation in the wet way.

Oxygen is always determined by difference in practice.

QUANTITATIVE DETERMINATIONS

Combustions for quantitative tests of carbon and hydrogen are made either by means of free oxygen or oxygen combined in cupric oxide. The former method is the ·more popular at present, although both have their advantages.

Combustion in ·Oxygen Gas. *a. In the absence of nitrogen.* Into a 12 to 15 mm. combustion tube from 60 cm. to a meter long, and open at both ends, place:

First. A roll of ignited copper gauze or foil, loosely fitting the tube, and about 25 cm. from one end.

Second. Coarsely granular copper oxide is filled into the tube to within 6 or 8 cm. of the open end. It is well to place a small loose plug of asbestos between the copper roll and the coarse copper oxide. The 6 or 8 cm., of empty tube is allowed to project from the furnace, a second asbestos plug retaining the copper oxide in place. If coarse oxide is not available, fine may be used. It is then necessary to gently tap the filled tube on a table to form a slight open channel through the top of the tube for the exit of gases.

Third. Wind a 10-cm. roll of copper gauze or foil about a piece of stiff copper wire, which may serve as a handle, and introduce the whole into the posterior open end of the tube.

Fourth. By means of a perforated rubber stopper connect the posterior end of the tube as it lies in the furnace with a train for purifying air or oxygen, consisting of two wash bottles of strong potassium hydroxide solution and two towers containing dry granular calcium chloride. One of the potash wash bottles may be replaced by a tower containing granular soda-lime if desired.

Fifth. By means of a similar perforated stopper, connect the anterior end of the tube to first a good-sized calcium chloride tube filled with granular calcium chloride, and weighed with plugs of short sections of glass rod attached by sections of rubber tubing, which are then removed and kept dry. This is in turn connected with, second, a Liebig or Geissler bulb filled with strong potassium hydroxide solution and fitted at its distal end to a smaller calcium chloride tube containing solid potassium hydroxide in small chunks, or soda-lime, both these latter having previously been weighed together, with the glass rod plugs as in the case of the calcium chloride tube. It is well to connect the whole absorption train to a final tube containing calcium chloride, which prevents any moisture being swept back from the air or aspirators.

Sixth. The train of absorption tubes is temporarily disconnected from the combustion tube and plugged, while the combustion tube itself is raised to redness, and the flames under it then extinguished. The plugs are now removed from the train and it is again connected to the distal end of the combustion tube. The stopper

is then removed from the back end, the roll of copper gauze on the wire withdrawn by means of crucible tongs, or pliers, a small boat containing a weighed amount of the material under examination (.200–.600 g.) introduced in its place, and the gauze roll immediately replaced just in front of the boat.

Seventh. The burners under the distal end of the combustion tube are lighted and the flame gradually carried back until the layer of copper oxide is all brought to a bright red heat. The burners at the front end of the furnace under the roll of copper gauze are next lighted and when this is also at a red heat, the burners under the boat containing the substance are also lighted, but kept turned down low at first until the substance is completely carbonized. All this time a slow current of purified and dried air has been forced or drawn through the apparatus at a rate which will furnish about two bubbles per second in the Geissler bulbs. Care must be taken to previously make sure that the entire apparatus is tight and that no backward current of the gases of combustion into the purifying train can take place. When the substance in the boat is seen to be carbonized the air current is replaced by one of similarly purified oxygen, which is allowed to pass at the same rate for about ten or fifteen minutes, or until the carbon is all burned, after which it is again replaced by the purified air, which is allowed to flow for about fifteen minutes more. During this latter period the burners may be turned down, or completely extinguished, as the air is simply to sweep the products of combustion out of the combustion tube and into the absorption train, and to again fill the latter with air instead of oxygen for reweighing. The calcium chloride tube, and the Geissler bulb with its attached

solid potash tube are now removed and placed in a
desiccator to cool, after which they are again stoppered
and reweighed. The increase in weight of the calcium
chloride tube, due to water from the hydrogen present
in the substance, multiplied by 0.1111 gives the hy-
drogen, and the increase in weight of the bulbs, due
to the carbon dioxide from the carbon, multiplied
by 0.2727, gives the carbon.

b. When Nitrogen is also Present. When nitrog-
enous compounds are under examination the com-
bustion tube needs to be from 100 to 150 mm. longer
than usual and is provided with a reduced copper
gauze or foil roll, which must be dry and bright, at
its distal end beyond the copper oxide, but within the
furnace so that it can be heated. While many text-
books direct the reduction of the copper by igniting
in a stream of hydrogen, the expedient previously
mentioned of plunging it into hot methyl alcohol and
drying thoroughly will be found more convenient
and safe, as in the previous case hydrogen is apt to be
occluded. In these cases the air is not replaced by
the oxygen gas until the last moment and is again
turned on as soon as the carbon is entirely consumed.
The copper as a rule is used but once, but may be re-
generated by subsequent ignition and reduction. It
prevents the absorption of nitric fumes by the potash.

In all combustions *the substance must be pure and
dry*. The errors which are most common are a too
low figure for carbon and a too high figure for hydrogen.
These are best prevented by having ample absorption
capacity to the potash bulbs and tubes on the one
hand, and in having the air, oxygen gas, contents of
the combustion tube, and the substance, made and
retained perfectly dry on the other.

Of late years a few combustion furnaces utilizing the heat formed by electrical resistance have appeared on the market, but their use will not vary much from the method just described.

In using the bomb method, a weighed amount of material, 0.200 to 1.200 g., compressed into a tablet, is placed in the tray, the wire which serves for combustion bent down so that it may touch it, the bomb closed and pumped up to a pressure of from 375 to 600 pounds, depending on the type of bomb and the amount of material taken, with oxygen gas previously purified by passing it first through a tube of copper oxide heated to redness and finally through an ample sized purifying train. Immerse the bomb in cold water. After passing the current to secure ignition, and allowing the products of combustion to become thoroughly cool, the gases are allowed to slowly escape through large filled calcium chloride tubes and potash bulbs as in combustions made with a furnace, the residual gases in the bomb, after the pressure has become normal, being washed out with purified air. The water due to the combustion of the hydrogen is partially carried out with the escaping gases and partly remains behind, condensed on the interior of the bomb wherefrom it must be absorbed by the calcium chloride, before proceeding to rinse the bomb out with water, and in the washings determine the organic sulphur, phosphorus, etc., which are present in the form of their oxyacids. The method as at present used presents few advantages over the old combustion-furnace method. Of late it has been found that very satisfactory results in organic combustions with air or oxygen may be obtained by using a short furnace, and tube containing some platinized asbestos beyond

the short layer of copper oxide. In these cases the beginning of the combustions should proceed very slowly.

Nitrogen. This common and important constituent of organic compounds is determined nearly always in a separate portion of the sample, the nitric fumes formed in the combustion for carbon and hydrogen as above described being reduced by the copper and escaping free into the air after passing the absorption train.

Nitrogen was formerly generally determined by the method of Varrentrapp, in which a portion of the substance, mixed with dry soda-lime, is heated in a tube filled with soda-lime in the combustion furnace, and the ammonia so formed swept out of the closed end of the tube and into an absorption tube containing standard acid by carbon dioxide formed from some dry oxalic acid contained in the extremity of the closed end and heated after the reaction proper is complete. While this method has much to recommend it, even at the present time, it has been generally superseded by various modifications of the original Kjeldahl method, which, however, is said sometimes to fail to give correct results with certain alkaloidal bodies, etc. It is carried out by introducing from 0.200 to 1.00 g. of the substance into a 500 cc. Kjeldahl flask of hard glass; 30 cc. of strong sulphuric acid and 1 g. of salicylic acid are then added (Gunning modification), the contents well shaken together and 5 g. of sodium thiosulphate added. The bottom of the flask is now heated cautiously by a low flame until all frothing ceases, and the heat then raised until the acid boils briskly and white fumes cease to escape (generally five to ten minutes); continue the heat now at such a rate as to insure the acid bubbling briskly until the contents of the flask are all of a pale amber color,

free from carbonaceous particles, then add intermittently a few crystals of potassium permanganate until the liquid is colorless or greenish from an excess of the permanganate, and continue the boiling until the sulphurous acid is expelled. The flask is now allowed to cool, an excess of strong solution of sodium hydroxide added, some fragments of metallic zinc introduced, and the liberate ammonia distilled slowly into a measured excess of standard acid, contained in a flask into which the delivery tube from the condenser dips. After the ammonia is surely all over the excess of acid is titrated with standard alkali and the amount of normal acid killed by the ammonia multiplied by 0.0140 will give the amount of nitrogen in the amount of substance taken.

Sulphur, Phosphorus, and the Halogens may all be determined by ignition in a nearly closed container with about ten times the amount of sodium peroxide as of material taken, as described under qualitative tests, but in some cases it will be found more convenient to heat with sodium carbonate and nitrate or with pure lime, or according to another wet method, to heat in a sealed glass tube with nitric acid to 150° C. for some hours. In either case the sulphuric, phosphoric, hydrochloric, hydrobromic, or hydriodic acid is separated and determined quantitatively as described under elementary inorganic methods. The same applies to metals, etc.

COMBUSTION WITH COPPER OXIDE ALONE

Where a supply of oxygen gas is not at hand, this older method of combustion will be found to be nearly equally satisfactory. The combustion tube used should be drawn out into a bayonet point at the front end,

which is either allowed to remain sealed together or closed with a rubber tube and clip. The management of the furnace is very similar to that in the former operation with oxygen and the use of the copper roll for reducing nitrous gases is the same, but much more essential. The details of the operation follow:

Pour about 10 cm. of the absolutely dry cupric oxide into the open end of the combustion tube and jar it down to the closed end, add the substance to be analyzed, which must be pure and dry, from a narrow weighing tube, taking care that it falls down the tube onto the copper oxide without sticking along the sides to any appreciable extent, cork and reweigh weighing tube to determine the amount of substance added, rinse down the combustion tube with another 10 cm. of dry copper oxide, and mix this and the substance intimately by means of a long copper wire bent into a single corkscrew turn at the end, but leaving about 4 cm. of copper oxide undisturbed at the closed end, then fill the tube with dry granular copper oxide to within 6 cm. of the open end, except in the case of nitrogenous substances, when sufficient room for the copper roll is left, and close the whole with a loose plug of asbestos. If granular copper oxide cannot be obtained the fine may be used, but then it becomes necessary to tap the filled tube gently on a table in order to form a slight channel along the top through which the gases of combustion may escape. Place the tube in the combustion furnace with the asbestos plug just beyond the reach of the flame, connect with the absorption train as in the combustion with oxygen gas, and heat first the distal, then the closed end, and finally that portion of the tube containing the mixture of the substance with cupric oxide. The

flow of bubbles should not exceed two per second through the potash solution, and the tube should finally be maintained at a bright red heat throughout, without, however, damaging the rubber stopper on one hand or allowing any moisture to condense in the distal end of the tube on the other. At last, when the combustion of the substance is complete, slip a rubber tube connected with the purifying train over the drawn-out bayonet end of the tube, make tight, and break off the glass end *inside the rubber tube after* a slight suction has been produced on the apparatus by an aspirator connected with the end of the absorption train. In this manner draw air slowly through the apparatus at the above rate until the gases of combustion have all been surely swept out of the combustion tube and into the absorption train, after which the parts of the latter are allowed to cool, stoppered and weighed as before.

In this last procedure the purified air serves only for completely emptying the combustion tube of the gases and should not be relied upon for completing the combustion, although it might of course help to do so.

Oxygen is practically always calculated from the difference between the sum of the other substances found and the amount of material taken.

We have all along been discussing the operations as commonly carried out on a fixed solid. In the case of liquids, especially when they are readily volatile, they are sucked into small thin tared glass bulbs made from glass tubing, sealed in a flame after the filling, cooled, and again weighed before introducing into the combustion tube. In the subsequent ignition, the heat bursts the bulb and allows the liquid to mix with the copper oxide.

Gases are analyzed by entirely different methods, a definite volume of organic gases being generally mixed with an excess of oxygen and exploded, after which the carbon dioxide formed from the carbon is absorbed by strong potash solution and its volume determined by the shrinkage in the volume of the whole. In like manner hydrogen may also be determined, although when free it is more often absorbed by spongy palladium. For more detailed accounts of these the beginner is referred to special works on gas analysis.

CHAPTER V

MOLECULAR WEIGHTS AND CHEMICAL FORMULÆ, ETC.

IT is obviously beyond the scope of this work to describe in detail the various methods used for determining these, and yet some passing remarks seem necessary in order to render the results arrived at in the preceding operations intelligible.

In the results of an organic combustion, the figures obtained represent the percentage composition of the substance, e.g., the combustion of 0.4714 g. of white needle-like crystals gave of carbon 0.1522, of hydrogen 0.0241, of nitrogen 0.0588, of bromine 0.01690, and of oxygen, by difference, 0.0673 g., corresponding to carbon 32.3%, hydrogen 5.1%, nitrogen 12.5%, bromine 35.9% and oxygen 14.2%.

The *relative* number of each kind of atom in the molecule is obtained by dividing these percentages by the corresponding atomic weight in each instance, which gives us for the above, carbon 2.6917, hydrogen 5.100, nitrogen 0.8929, bromine 0.4487, and oxygen 0.8880, but while these figures may represent the *relative* number of atoms, it is considered impossible for fractions of an atom to exist in one molecule, and so, the greatest common divisor of these several numbers is found, as closely as possible, and by dividing the numbers by this we obtain the most simple proportion in which these atoms could exist in the above compound.

Allowing for slight errors in the actual analysis which are almost always present, we arrive at carbon 6, hydrogen 11, nitrogen 2, bromine 1, oxygen 2, as representing the simplest formula which could be assigned to this compound.

But the above formula or one represented by any multiple of it might just as reasonably be the correct one, as we have as yet no assurance whatever that the molecule of this substance contains but one atom of bromine. In order to determine these we must first determine the molecular weight of the compound and then we shall be in a position to adjust our figures accordingly. The most commonly used methods in vogue for this purpose at present are the vapor density method according to Victor Meyer and the depression of the freezing-point method according to Beckmann. The former method, which is generally the preferable one when the substance can be converted into vapor without decomposition, is carried out by employing a long tube expanded into an elongated bulb at the bottom, corked at the top, and provided with a capillary side outlet near the top which dips below the surface of water or mercury in a trough and may at will be moved under a filled and inverted gas-measuring tube which stands in the latter. The long bulb tube is heated by means of a jacket and the vapors of some suitable liquid having a boiling point above that of the substance being investigated. When all is in equilibrium the outlet tube is moved beneath the gas-measuring tube and a weighed portion of the substance is dropped into the hot tube by means of a suitable mechanical arrangement attached to the cork. All of the material immediately becomes vaporized and displaces an amount of air into the gas tube correspond-

ing to the volume occupied by the vapor of the sub-
stance at the temperature employed. In order to
make all comparisons on the same basis as regards
pressure and temperature the volume of vapor finally
measured is reduced by calculations to the volume
which it would occupy at zero centigrade and at 760
mm. barometric pressure, when the vapor density
may be found by comparing it with hydrogen. As,
according to Avogadro's law, equal volumes of all
gases or vapors under like conditions contain a like
number of molecules, it is evident that the molecular
weight relative to that of hydrogen as two, is easily
found; being generally one-half of the specific gravity
or density.

Unfortunately many substances may not be converted
into vapors without decomposition or dissociation, and
other means have to be employed. In the case of
organic bases or acids, these may be combined with
mineral acids or bases of known composition and the
molecular weight of the organic body thus learned by
analysis.

In many cases, however, another appeal to a purely
physical process has to be made in the form of a deter-
mination of the *lowering of the freezing point* of some
suitable solvent, by a known amount of the substance
under investigation. The apparatus employed is gen-
erally that of Beckmann and consists of an accurate
thermometer having an adjustable scale and reading to
hundredths of a degree, which is inserted into a deep
test tube having a broad side arm opening off the top,
a platinum wire stirrer, and having outside it another
larger test tube which allows of an air space always
surrounding the inner one for the purpose of insuring
uniform temperature changes. Into the inner tube is

poured from 10 to 20 g. of a suitable solvent weighed accurately to 5 mg., the bulb of the thermometer introduced into the liquid, the outer tube surrounded by a suitable freezing mixture, the stirrer agitated, and when the temperature has fallen about to the freezing point indicated by the scale of the thermometer being used, a small crystal of the previously frozen solvent is dropped through the side arm of the tube, when freezing will generally immediately ensue with a *rise* of temperature generally amounting to several tenths of a degree. The maximum temperature observed after this rise is the true freezing point and the determination is repeated until the results are certain. The solvent is again allowed to melt and a portion of the material under examination, accurately weighed to milligrammes, introduced through the side arm and allowed to dissolve completely when the freezing point of the mixture is again determined, and with it the lowering caused by the introduction of the substance. A correction has sometimes to be made for the added amount of crystallized solvent introduced to bring about freezing.

The molecular weight is calculated from the following formula: M equals C times P, divided by t. Where M is the molecular weight sought, C is a constant varying for each solvent generally used, P is the weight in grammes of the substance in one hundred grammes of the solvent, and t is the observed depression of the freezing point. The constants for some of the most commonly used solvents are glacial acetic acid 39, benzene 49, phenol 76, water 19.

In the case of our substance which we are here investigating, 0.3095 g. added to 15.470 g. of glacial acetic acid lowered the freezing point by 0.35°, and by this method the molecular weight is found to be 223, which

corresponds with the formula having one bromine atom in the molecule. The formula for our compound is consequently $C_6H_{11}N_2BrO_2$. An error of 5% is not uncommon in the freezing-point method.

The following preliminary examinations, and condensed methods for estimating various atomic groups in organic compounds may, however, serve as a guide to the analyst or student in obtaining more information regarding the composition and structure of these bodies than is furnished by a simple elementary analysis, and in more advanced pharmacological work, as for example in studying the relations between chemical constitution and physiological action, these furnish much of the information which is absolutely essential.

1. Ignite in a tube with soda lime and pass the gaseous products through dilute hydrochloric acid. The acid retains any ammonia from the nitrogen of the compound, and frequently such bodies as pyridine, benzene, etc., which escape undecomposed. The other gaseous products which are not absorbed or condensed in the acid solution are to be collected in a gas tube and further examined. These latter may consist of carbon dioxide, methane, etc. This treatment will often resolve compounds, particularly acids, into their parent hydrocarbon (methane, benzene, etc.), together with other decomposition products. If this attempt is unsuccessful, the similar ignition of the body with zinc dust will be desirable.

2. Fuse with potassium hydroxide in an oil bath, dissolve the melt in water, partly neutralize with acid, extract with ether. Render now distinctly acid and again extract with ether. Bodies formed by this decomposition will often indicate something of the nature of the original material. Similar results may sometimes be obtained

by simply boiling for some time with KOH solution. In this case care must be exercised to prevent the unnoticed escape of volatile bodies as, e.g., methyl alcohol from methyl salicylate. Acids formed may be treated as in (1).

3. Boil for some time with quite strong hydrochloric acid, dilute with water, extract with ether, and examine both the ether extract residue and aqueous solution. By this operation there may be formed esters from alcohols, furfural from carbohydrates, glucose and other bodies from glucosides, etc.

4. Oxidize the substance by boiling with potassium permanganate and with sulphuric acid and potassium dichromate, also reduce it with tin or zinc and hydrochloric acid. Characteristic products are sometimes formed by these operations, frequently acids, aldehydes or ketones, etc., by the former, and alcohols, aldehydes, amines, etc., by the latter.

5. Attempts at nitrifying with a mixture of nitric acid one part and sulphuric acid three parts, carefully controlling the temperature, should be made. Also an attempt at sulfonating with strong sulphuric acid. This treatment will distinguish, for example, between the saturated hydrocarbons of the methane series which are unaffected, and the hydrocarbons of the benzene series or the unsaturated hydrocarbons of the methane series, which combine.

6. If soluble, test with alkaloidal reagents for alkaloids and similar basic bodies, ferric chloride and bromine water, which give characteristic color reactions and precipitates with most phenol-like bodies, etc., barium chloride, lead acetate, and silver nitrate for precipitates from acidic bodies, etc.

7. If possible determine the optical properties,

rotation of the plane of polarized light, refractive index, spectrum if colored, and fluorescence.

The following paragraphs will give a hasty review of the methods most commonly employed in determining various organic atomic groups or rests:

Hydroxyl (OH). Acetylate with acetyl chloride, acetic anhydride, or glacial acetic acid and sodium acetate; or benzoylate with benzoyl chloride, benzoic anhydride, or phenyl sulphonic chloride. Then hydrolyze the resulting compound by boiling with water, dilute alkaline or dilute acid solutions, and titrate the acid (acetic or benzoic) formed. The acid formed is, as will readily be seen, a measure of the hydroxyl groups in the weighed original substance which were necessary to produce this acid.

Carbonyl (CO). (a) Warm with phenylhydrazine and glacial acetic acid and weigh the resulting phenyl hydrazones, or use an excess of phenylhydrazine and afterward decompose this excess by oxidation with boiling Fehling's solution, and measure the liberated nitrogen.

(b) Allow the compound to react with hydroxylamine and weigh the resulting oximes. This determination is most often used in the investigation of aldehydes and ketones and their derivatives.

Methoxyl (CH_3O) and Ethoxyl (C_2H_5O), Zeissel's method. Heat the compound with strong hydriodic acid in a current of carbon dioxide and pass the formed methyl iodide (or ethyl iodide) slowly through an inverted condenser surrounded by water at 40 or 50° C. (or 80° C.), then potash bulbs containing red phosphorus or arsenic anhydride, and finally through wash flasks containing alcoholic silver nitrate solution. The silver solution is then treated with water and a drop of

nitric acid and evaporated until the silver iodide separates.

One Hundred parts of silver iodide so formed are equivalent to thirteen and twenty-hundredths parts (13.20) of methoxyl or to nineteen and twenty-one-hundredths parts (19.21) of ethoxyl.

Carboxyl (CO—OH). This group, which is the essential characteristic one in all organic acids, may be determined by titration of the free bodies, analysis of salts, esterification by heating with alcohols, etc., and by determination of electrolytic conductivity or the amount of carbon dioxide evolved from carbonates.

Amino (NH₂). (*a*) In aliphatic compounds. Treat the sulphuric acid solution in an atmosphere of carbon dioxide, with sodium nitrite (NaNO₂) and pass the evolved gases through a potash bulb containing 3% alkaline permanganate solution and collect the evolved gas (nitrogen) with carbon dioxide, and absorb the latter with KOH solution. Another method is to analyze the salts or double salts with heavy metals.

(*b*) In aromatic compounds. The *salts* may be titrated *directly* in hydro-alcoholic solution, using phenolphthalein, rosolic acid, or cochineal. Or prepare the diazo derivative by titrating the dilute hydrochloric acid solution of the base at zero C., with tenth normal sodium nitrite (NaNO₂) using potassium iodide starch paper as indicator. The base may also be *directly* converted into a diazo dye by pouring the ice-cold hydrochloric acid solution containing sufficient sodium nitrite into a measured quantity of 2, 3, 6 naphthol disulphonate ("R" salt), containing the equivalent of about 1% of naphthol with an excess of sodium carbonate. Precipitate the dye with sodium chloride, wash, weigh, and determine, if necessary by

another experiment, the volume of the *titrated* "R" salt solution necessary to combine with the diazo derivative of the original base. The salts and double salts may also be analyzed as in the case of the aliphatic amines.

Amido (CO—NH₂). (*a*) Hydrolyze by prolonged boiling with hydrochloric acid (sometimes alkali), add excess of sodium hydroxide and distill off and titrate the resulting ammonia. (*b*) Warm with sulphuric acid (5 parts), cool to zero and add one part of sodium nitrite (NaNO₂) in ice-cold water *very* slowly, warm to 60 or 70° C., when nitrogen gas is evolved, and continue heating to 80 or 90° C. for several minutes, cool *strongly*, collect the precipitate, purify by solution in alkali and reprecipitation with acid. The evolved nitrogen may be measured.

Nitrile (C—N). Boil for a considerable time with hydrochloric acid, add alkali, and distill off the formed ammonia (or acid) which may be estimated.

Imino (N—H). (*a*) Analyze salts. (*b*) Acetylate with acetic anhydride, dilute with water, and titrate the acid formed. Hydrolyze by prolonged boiling with hydrochloric acid, add alkali and distill off the formed ammonia.

Diazo (N—N). (*a*) Aliphatic. Add the compound to well-boiled highly dilute sulphuric acid in a nitrometer, heat to boiling and measure the evolved nitrogen gas. If amino groups are also present, their salts will remain in the mixing flask.

Titrate the ethereal solution of the diazo compound with ethereal solution of iodine until the color changes from yellow to red. $(RN : NR + I_2 = RI_2R + N_2)$.

(*b*) Aromatic compounds. Determine in a Lunge nitrometer in the wet way, using 40% sulphuric acid.

Hydrazide (NH—NH₂). Oxidize by boiling with Fehling's solution, and collect and measure the evolved nitrogen gas. (*b*) Titrate with tenth normal iodine in excess $(C_6H_5NH.NH_2 + 4I = 3HI + 2N + C_6H_5I)$.

Nitro (NO₂). Titrate to the amino compounds with stannous chloride in excess, in hydrochloric solution, and calculate from the equation

$$R—NO_2 + 3SnCl_2 + 6HCl = R.NH_2 + 3SnCl_4 = + 2H_2O.$$
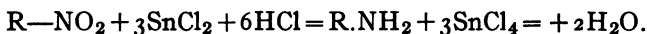
Reduce by the diazo compound with tin and hydrochloric acid and treatment with about the theoretical quantity of sodium nitrite $(NaNO_2)$ and fine copper without removal of the tin.

Nitroso (NO). Decompose the substance with an excess of phenylhydrazine in strong acetic acid, in a current of carbon dioxide, by gentle warming, and collect the evolved nitrogen gas over KOH solution.

$$(R—NO + C_6H_5NH.NH_2 = R.N + H_2O + C_6H_6 + 2N.).$$
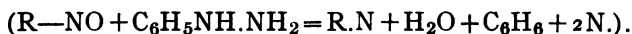
Peroxide (O—O). Titrate with stannous chloride in excess.

Iodoso (I—O) and Iodoxy (I—O₂). Liberate iodine from potassium iodide in acid solution and titrate with sodium thiosulphate. Prolonged heating in a closed vessel in a water bath is required.

CHAPTER VI

PRINCIPLES OF DRUG ANALYSIS. METHODS.

THE term drug is here used in the more restricted sense defined in the introduction for the reason that the methods of crude vegetable drug analysis might be said to fairly represent most of the special problems presented to the analyst of medicines generally, as the separation and determination of the various inorganic bodies and of such commonly used organic ones as alcohol, sugars, glycerin, etc., are familiar to every chemical worker, and for the reason that most of the organic synthetic remedies may as a rule be separated by methods essentially the same as those employed in phytochemistry.

Drug testing requires some methods distinctively its own, but depends mostly on a knowledge of ordinary inorganic analysis, phytochemistry, micro-pharmacognosy, and experimental pharmocology.

The analysis of a medicinal compound or mixture is generally performed for one of two purposes. Either one or more active principles in a known substance are required to be accurately estimated for purposes of standardization, proof of purity, commercial valuation, or in chemico-legal cases, in which cases it may perhaps more properly be called an assay, or, all of the essential ingredients of an unknown medicine are required to be at least approximately separated and determined where this is possible for the purpose of obtaining some

97

idea of the relative merits or demerits of the mixture, or perhaps for the purpose of duplication. While this latter is vastly more difficult of accomplishment than the former, and in the present state of our knowledge often impossible, quantitative accuracy is generally less important. Familiarity with the uses and properties of the ingredients found will enable one to judge of the quantities likely to be used, especially as the doses of most medicines follow more or less arbitrary limits, e.g., if from each 5 cc. of a mixture are separated 7.5 mg. of morphine calculated as sulphate, it will be reasonable to suppose that each teaspoonful was intended to contain 8.0 mg. (⅛ grain), as this is a common dose of that alkaloidal salt.

Operations of the former class are given relatively less attention in this work as, in the case of most of the important regular official medicinal substances at least, authoritative legal standards and tests are given in the Pharmacopœias.

For the latter class no hard and fast rules can be laid down. The treatment of each substance or mixture is to a certain extent a law unto itself and the success of the drug analyst will largely depend on the ingenuity with which he is able to meet these varying requirements, but as little or no advancement is possible without some systematically outlined method of procedure such a course is provided in the following pages, with the understanding as above stated that variations in the expected results will frequently occur, due to varying physical conditions and accompanying substances.

Most of the pharmacologically active bodies occurring in vegetable drugs occur in relatively small quantities as volatile oils, fats, resins, tannins, phlobaphenes, plant acids, glucosides, alkaloids, or unorganized ferments,

and are accompanied in the drug by much larger quantities of inert matters such as starches, gums, sugars and other cellulose derivatives, proteins, coloring matters and that large class of bodies generally classed under the indefinite name of "extractives," all of which are of more importance to agriculture. All of the first class except the ferments are more or less soluble in alcohol of various strengths, but by far the greater amount of inert stuff is left behind, and a goodly amount of that which does dissolve, e.g., "extractives," afterward becomes insoluble and is deposited during the various manipulations. We have here not only a rational explanation of the use of alcohol in preparing medicinal tinctures, fluid extracts, etc., but also apparently the most common solvent for all of those bodies in which we are here particularly interested, with the few exceptions previously stated, so "*The drug or solid medicinal residue should be extracted, warm, with the strongest alcohol in which all of the pharmacologically active bodies are soluble.*" In practice the result is often best obtained by extracting first with very strong or even absolute alcohol and completing the process with that of 75 or 80% strength, and finally mixing the extracts. Only in the case of some especially fatty drugs like certain seeds, etc., is it necessary or in most cases desirable, to first extract the fats with petroleum ether before extracting with the alcohol. In the latter instance it is necessary to finally again extract the fatty residue left by the evaporation of the petroleum ether by digestion with 75% alcohol, which alcoholic extract is finally added to the principal one.

In the next step to be followed, nearly all of the methods so far advanced have two principles in common, first, the so-called "resinoids," which include fats,

waxes, resins, phlobaphenes, etc., all insoluble in water, are first excluded from the water-soluble portion by taking up the residue from the evaporation at low temperature of the original alcoholic extract, with water or weak alcohol, and second, the separation of the latter into groups having primarily more or less acidic or basic properties by extracting first acid and then alkaline solutions, or by precipitating with first normal and then basic lead acetate. In either case the bodies thus separated are further isolated by treatment with a succession of solvents.

One of the first of these schemes, applied particularly to the separation of alkaloids, was the Stas-Otto method, which depended on shaking out first an acid and then an alkaline aqueous liquid by ether. This method was afterward elaborated by Dr. Dragendorff of Dorpat, who completed his separations by shaking out in succession the acid water solution with petroleum ether, coal-tar benzene, and chloroform. The dissolved portions of these several solvents were then extracted by shaking out again with petroleum ether, the liquid made alkaline by ammonia and then again extracted by shaking out in succession with petroleum ether, benzene, chloroform and amyl alcohol. About the same time Mr. H. B. Parsons of the United States Department of Agriculture published a scheme depending more on the use of normal and basic lead acetates, an operation which was also sometimes used by Dragendorff. He also preferred to extract the original drug with a succession of solvents before the lead treatment.

All of these methods have several serious disadvantages. First, a number of important bodies will generally be found unequally distributed in the residues from several of the solvents used for extraction, instead of

being confined to a single one. Second, neither the extraction by immiscible solvents nor the precipitations by normal and basic lead acetate will furnish sharp separations of the groups, and in the case of the latter, there is the added difficulty of freeing the filtrate from lead without loss or injury to certain organic constituents, and without complicating a possible subsequent inorganic analysis, where an account of a small sample this requires to be done on the same lot of material.

Third, the lead precipitates are not entirely insoluble in the liquids in which they are formed. On the other hand, the lead method gives much better results in some cases, especially when dealing with certain bodies like glucosides, tannins, etc., than does the extraction with immiscible solvents alone, and where the material consists quite largely of vegetable matters, as in crude drug analyses, and a preliminary test has shown the lead salts to precipitate a considerable amount of organic material, and especially when there are not also present quantities of sulphates, chlorides, carbonates, phosphates, etc., which precipitate lead, it is well to use a scheme embodying both methods. In other cases some modification of the original Dragendorff method still continues to furnish best results with the least expenditure of time and especially when a subsequent search for mineral matters is required on the same lot of sample.

From a somewhat extended experience with both of these, the writer believes that with any method, to obtain the best results in the most direct manner when working on unknown crude drugs "the pharmacologically active organic bodies should all be first extracted from the major portion of the inert residue or mineral substance by a single general solvent for the former, separated

as completely as possible into groups, the members of which shall have more or less common properties, the bodies of each group further separated by treatment with a regular succession of suitable solvents, proceeding from the special (e.g., petroleum ether) to the more general (e.g., ethyl ether), and finally isolated and purified by fractional crystallization whenever this is possible, for the determination of their weight; and their identity established by melting point determinations (or boiling-point determinations), color reactions, solubilities, etc., and in some cases their elementary composition. Any mineral matters or organized residue from the original extraction are subjected to the customary ultimate inorganic analysis or identified microscopically. The volatile and physiologically inert organic bodies are determined as usual when desirable."

The following is a more detailed statement:

Moisture. This may be determined by drying from 3 to 5 g. of the finely ground drug, to constant weight in a tared dish at 100° C. A method favored by some chemists where the drug is to be afterward exhausted in a continuous extraction apparatus, is to pack the powder in a tared finely perforated tube for drying which is finally put directly into the extraction apparatus after the drying operation. This direct heating of course drives off other volatile matters than water where these are present, and where this error is not allowable and in any case where sufficient time can be spared, it is better to allow the dish containing the powder to stand for some days in a desiccator over *strong* sulphuric acid until between successive weighings the weight remains constant.

Ash. Mineral ash may be determined in some cases

by directly burning two or three grammes of the mixed sample in a tared crucible or dish at a low red heat until the ash remains white or grayish white. Where the carbonaceous residue fails to be completely consumed owing to its failure to settle sufficiently close to the wall of the crucible, this may often be remedied by allowing the latter to cool, distributing a few drops of ammonium nitrate solution or nitric acid over the contents in such a way as to uniformly moisten the whole, drying cautiously, and again cautiously igniting. As this process of determining ash subjects the material to a heat which is likely to volatilize some of the alkalies, notably potassium, it is always safer and in some cases even quicker, to at first thoroughly carbonize the mass, extract it with water, completely incinerate the residue at a higher heat, evaporate the aqueous solution in the crucible and again ignite cautiously for weight.

The ash, when desirable, may be examined for its constituents according to the methods of inorganic analysis, bearing in mind the fact that previous salts of organic acids and nitrates will now exist as carbonates unless nitric acid was used to complete the ignition, and that ammonium and other volatile compounds are of course lost. It is sometimes well to examine the portions which are soluble in water and dilute hydrochloric acid and insoluble separately.

Where such volatile bodies as arsenic, mercury, ammonium, etc., are also present, as in some mixtures, the method described in Chapter III, under destruction of organic matter, should be followed.

Generally the ash of crude drugs alone will contain only small amounts of silica, aluminum, iron, calcium, magnesium, potassium, and sodium, with phosphoric,

sulphuric, carbonic, and hydrochloric acids, and furnishes little information to the drug analyst.

Extraction. A suitable quantity of the drug in dry fine powder is extracted with alcohol according to some one of the methods described in Chapter II. The proper amount to be used will depend on circumstances. Ten or twenty grammes will generally furnish an idea of the general nature and the relative amounts of the more important constituents, but as the quantity of some of these is frequently less than one-tenth of one per cent, it is necessary to extract at least one hundred grammes in order to obtain sufficient quantities of these for any considerable amount of qualitative study; and if in addition, it becomes necessary or desirable to make an elementary organic analysis and study of the structure of the separated bodies, as in dealing with new or unstudied drugs, etc., it may be necessary to employ one or more kilogrammes of the crude drug, the quantity to be used being generally indicated by a preliminary examination of a smaller sample.

For exhausting small lots of drug, any of the common forms of continuous extraction apparatus described in Chapter II may be used. The type shown in Fig. 2 is especially serviceable for lots of 100 g. or more, especially as the injury due to heating may be minimized by reducing the pressure, but for this as well as for larger quantities, simple percolation or maceration followed by percolation in a warm chamber offers the safest and frequently the least troublesome method. The drug is extracted first with warm strong, preferably absolute alcohol, and finally at room temperature with 75 or 80% alcohol. Complete extraction can be judged in most cases by the absence of color or taste in the extract, but in case of doubt a few drops may be

allowed to evaporate in a watch-glass for the presence of any solid residue. In using any form of continuous hot-extraction apparatus, it is always well to shortly remove the first portion of extract which contains most of the active constituents, before it has been subjected to much heating and then complete the extraction with fresh solvent. In the single case of oily or especially waxy drugs is it necessary to first extract these bodies with petroleum ether.

Evaporation of the Extract. The alcoholic extracts are received in the same strong flask, and the alcohol and volatile matters distilled off under diminished pressure at the lowest practicable water-bath temperature. The arrangement shown in Fig. 4 answers well for this purpose. In those cases where it has been necessary to first extract with petroleum ether, the weighed residue in the dry-air current desiccator is thoroughly worked up with 75% alcohol and this extract and washings added to the main extract before distilling off the solvent. Where no volatile matters are to be determined in the drug, the alcohol may be allowed to evaporate spontaneously at a moderate heat in a broad tared dish. After the solvent is entirely driven off, the tared flask or dish is allowed to stand in a desiccator until constant, and weighed as *total alcoholic extract*.

The alcoholic distillate is set one side for the possible determination of *volatile matters*.

Soluble Solids. The dry alcoholic extract in the bottom of the flask is heated with an amount equal to one-half the weight of crude drug originally taken, of strong alcohol, thoroughly worked up by means of a stout rod, treated with four times this amount of hot water (about 75° C.) giving an alcoholic strength of about 20%, a weighed amount of ground pumice stone,

talc, or other insoluble material added, the whole stirred well together for some time, when the "resinoids" have become somewhat agglutinated around the pumice particles, filtered hot and washed somewhat with hot water. The residue on the filter is again digested with alcohol, pumice stone, and four times the amount of water added, filtered this time through a tared filter and well washed. It is only by repeated solution in alcohol and precipitation with water that all of the water-soluble bodies may be extracted from the resinoids. If on cooling this water solution deposits any bodies, they are to be filtered off and examined later. The resinoid precipitate is dried at a moderate heat, or in a desiccator, weighed, and the tare of the filter and added pumice deducted.

Lead Acetate Precipitate. The filtrate and washings from the resinoid precipitate are evaporated somewhat at low temperature and treated with a slight excess of 25% lead acetate solution, added gradually and with constant stirring. The flask is allowed to stand some time, the precipitate collected on a filter, and if at all considerable washed back into the original flask with fresh water and again collected on the filter and washed with water containing a little normal lead acetate.

Basic Lead Acetate Precipitate. The filtrate and washings from the normal lead acetate precipitate are treated with a little litharge, warmed to about 60° C., and treated with a slight excess of 25% solution of basic lead acetate gradually added and stirred at frequent intervals for some time, after which it is allowed to settle somewhat, collected on a filter, washed back with water, again collected and washed with water containing a little of the precipitant.

Freeing the Filtrate from Lead. The filtrate and washings from the basic lead acetate precipitate are now treated with some alcohol, and hydrogen sulphide passed through the liquid until the lead is all precipitated, filtered, and the lead sulphide precipitate washed somewhat with 20% alcohol, then with water, and the whole amount of filtrate freed from excess of hydrogen sulphide by blowing a current of carbon dioxide or air through the liquid. If it is markedly acid in reaction this is *nearly* neutralized by sodium carbonate or calcium carbonate. The whole is then concentrated, either by careful open evaporation or by means of a partial vacuum until the alcohol is all removed and the liquid reduced about to the weight of the original drug taken, and measured.

Precipitation of Alkaloids. A small aliquot portion of the liquid is removed by means of a pipette and distributed in drops on a clean glass surface placed over black paper and each drop tested with a small drop of one of the common reagents for alkaloids. As reagents, Meyer's potassio-mercuric iodide, Thresh's potassio-bismuthic iodide, phospho-molybdic and phospho-tungstic acids, iodine in potassium iodide, mercuric, auric and platinic chlorides, picric acid, and fixed alkalies are to be recommended. If a number of these produce distinctly visible precipitates, it not only indicates the presence of alkaloids but also indicates their precipitants, and generally suggests the best reagent to use for separating the entire amount. This is generally Mayer's reagent or phospho-molybdic acid.

If alkaloids are absent (small amounts of some difficultly soluble bases may be retained by the basic lead acetate precipitate) the main portion of liquid is directly evaporated at a low heat for the final residue.

If they are present, the main portion of the liquid is slightly acidulated with hydrochloric and treated gradually with a slight excess of the chosen reagent, added drop by drop with constant stirring. The alkaloidal precipitate is filtered off and washed with a little water. The fact must not be lost sight of that under the conditions here described, other bodies than alkaloids may give slight precipitates with many of the commonly used alkaloidal reagents.

The filtrate must now be freed from the excess of alkaloidal reagent used, by a treatment which will from necessity vary with circumstances. If phospho-molybdic acid has been used, it may be decomposed by simply adding an excess of alkali followed by a slight excess of acetic acid: if by Mayer's reagent, by adding stannous chloride solution, warming, adding sodium hydroxide solution in very slight excess and finally an excess of acetic acid, or by passing hydrogen sulphide and the iodine removed from the filtrate by adding sodium thiosulphate.

However freed, the filtrate is finally evaporated at a low heat—preferably in the vacuum apparatus—to a small bulk, a quantity of clean dry sand added, and the evaporation continued, stirring as required to secure uniformity until the mass is dry and uniformly distributed over the sand particles. During this evaporation the reaction of the liquid must be *faintly* acid with acetic acid but free from any mineral acid.

As an alternative procedure the liquid may be evaporated to the proper volume, saturated with salt and shaken out with the immiscible solvents, to be described later, instead of the complete evaporation and dry extraction.

Volatile Matters are generally best determined by

distilling a quantity of the original material with steam until it ceases to carry over further appreciable quantities of material, saturating the distillate with salt and shaking out with light petroleum ether, boiling-point 30 to 60° C., and allowing the separates to evaporate in the dry air current desiccator as described in Chapter II. Where the small size of the sample will not allow of this, the distillate from the alcoholic extract may sometimes be considerably diluted with water, saturated with salt and similarly extracted.

We have now separated our original alcoholic extract, which we have reason to suppose contained all of the pharmacologically important bodies of the drug (with the exception of ferments and other bodies related to the proteins) into *six groups:* I. Those precipitated by and insoluble in water, the so-called " resinoids," consisting principally of fats, wax, resins, phlobaphenes, chlorophyll, and other colors; II. Those precipitated by normal lead acetate, consisting principally of plant acids, tannins, salts of the ash, extractives, colors, glucosides, etc.; III. Those precipitated by basic lead acetate, consisting of more colors and extractives, other more basic or neutral glucosides, and sometimes traces of alkaloids; IV. Those precipitated by alkaloidal reagents, in other words alkaloids or at least basic organic substances; V. Those neutral bodies in the final filtrate, glucosides, sugars, etc.; and, VI. Those volatile with steam, consisting of volatile oils, camphors, volatile acids and alkaloids.

SEPARATION OF THE MEMBERS OF THE SIX GROUPS

I. The dried resinoid residue is rubbed into powder in a mortar and together with the added insoluble mineral matters, packed very loosely in a convenient extractor and exhausted in succession with petroleum ether, benzene, chloroform, ether and strong alcohol, and the several solutions evaporated in tared dishes for weight.

The petroleum ether solution will consist principally of fats, with perhaps small amounts of waxes, and in the case of green drugs will also contain portions of the chlorophyll, which is also distributed through the other solutions. The benzene solution will contain any remaining portions of waxes and certain resins. The chloroform and ether may extract further resins, and alcohol will further dissolve phlobaphenes, bodies split off from the tannins and which are also soluble in ammonia water.

It must not be presumed that the separations by these solvents are as a rule sharply defined, nor can this be expected from the known physical properties of dissolved organic bodies, but the separations are always much sharper than those which can as· a rule be obtained from the evaporation of a single solvent. In the case of mixtures containing the newer organic synthetic compounds, this water-insoluble portion is often of the utmost importance, as many of this class are here to be separated by careful fractional crystallization, from one or more of the various solvents.

II. The lead acetate precipitate is rubbed in a mortar with a slight excess of 10% sodium carbonate solution gradually added until all of the organic matters are in

solution and the lead carbonate settles entirely free, and filtered. The solution is now to be successively extracted with chloroform or benzene, ether, acetic ether and, finally, with about 75% alcohol. This may be accomplished by slightly acidulating it with dilute sulphuric acid, saturating with sodium sulphate, and either " shaking out " with the various solvents in a separator or continuously extracting in a perforator. Or, as in the case of the final residue, evaporate the solution—acidified slightly with acetic acid instead of sulphuric acid—with sand and extract dry with the solvents named. The enumeration of some of the plant bodies likely to be found in the residues from these solvents is given in the tables farther on. After the extractions with immiscible solvents in the wet way, the water solution may still contain all or some of those bodies which alcohol would have extracted in the dry way, and if these are to be separated the solution must still be dried and the alcohol applied as usual. The final residue will always still yield certain extractives to water.

III. The basic lead acetate precipitate is triturated in a mortar with an excess of acetic acid until dissolved, (with the possible exception of some of the litharge) 10% solution of sodium carbonate added in quantities sufficient to precipitate all of the lead, filtered, any remaining lead removed if necessary by hydrogen sulphide, the latter being finally blown out, and the various glucosides, colors, etc., extracted in the same manner as were those of the lead acetate precipitate, by using in succession benzene, chloroform, ether containing 25% alcohol, and finally with alcohol alone. Water will here again remove certain extractives from the final residue. For the bodies extracted by these

solvents see Table I. In careful analyses one must never omit the search for some alkaloids in this fraction, which is generally best done by shaking out a small portion of the final clear aqueous liquid while still alkaline from the sodium carbonate, with chloroform one part and ether four parts, allowing this "separate" to evaporate and testing the slightly acidified residue with some of the previously mentioned alkaloidal reagents.

IV. The alkaloidal precipitate requires, like the lead ones, to first be decomposed by a proper reagent. If the precipitation was made with Mayer's reagent, the precipitate may be triturated with stannous chloride solution, a slight excess of soda solution added and finally a slight excess of dilute sulphuric acid. If phospho-molybdic, phospho-tungstic or some other reagents were used it may only be necessary to decompose the precipitate with a slight excess of soda or barium hydroxide before adding a further slight excess of the dilute sulphuric acid.

Mayer's reagent and some others formed from heavy metals may also be decomposed by suspending them in water and passing hydrogen sulphide. By whatever process obtained, the aqueous acid solution is filtered into a separator or perforator and extracted in *acid* solution with *benzene*. It is then made *alkaline* with ammonia and extracted successively with petroleum benzin, coal-tar benzene, chloroform, and after saturating the solution with sodium sulphate, chloroform three parts and alcohol one part, using each as long as it is seen to extract anything, and finally dissolving the residues left by the evaporation of these several separates in a slight excess of 1% sulphuric or hydrochloric acid, to which solution the tests for identity

are applied. This is generally effected by treating very small portions in small tubes with such general precipitants as have been mentioned, especially gold chloride, platinic chloride, picric acid, and iodine, as these are generally most apt to furnish compounds crystallizing well and whose melting points and other physical properties have been recorded. The best crystals are often obtained by dissolving the precipitate in alcohol, the evaporation of which leaves well-defined forms. Color reactions, etc., are also observed by allowing separate drops to evaporate on glass or white porcelain and treating the residues with such reagents as strong sulphuric acid, nitric acid, sulphuric followed by nitric acid, sulphuric acid and cane sugar, sulphuric acid and molybdic oxide, etc., both in the cold and on warming. For bodies extracted see Table I.

The final filtrate or dry residue, after separating the alkaloids and the excess of alkaloidal residue as described before is extracted as were the lead precipitates in succession with chloroform, ether three parts and alcohol one part, and finally with alcohol. For the bodies possibly present here see Table I.

After being sure that all active bodies have been extracted from the final residue, this may be further examined for extractives, sugars, etc., or it may be retained and added to a subsequent water extract of the original drug where one is made, for the estimation of these bodies, starch, gum, pectin bodies, etc.

Volatile matters, which as before stated are generally best separated from a fresh lot of material by steam distillation, accumulate with a large excess of condensed water. The distillate, or an aliquot portion of it, is treated with a few drops of phenolphthalein or cochineal solution and titrated with tenth normal

sodium hydroxide solution for total acidity. If the reaction should be alkaline, this might be due to the presence of a free volatile alkaloid. A slight excess of alkali is then added, the liquid saturated with salt, and completely extracted by shaking out with low boiling petroleum ether (30° C. to 50° C.) which after standing for complete settling is allowed to evaporate in a tared dish in the dry air current desiccator as previously described for weight. The petroleum ether must be distilled carefully until it ceases to leave any appreciable residue, when 100 c.c. or more are evaporated to dryness. The saturated distillate is now slightly acidified with sulphuric acid and shaken out with ether for the recovery of the acids. The weighed petroleum ether residue is treated with a small amount of 1% hydrochloric acid for the recovery of the volatile alkaloids if present, which will be taken up as hydrochlorides leaving the volatile oils, etc., to separate and be removed by a pipette. The alkaloidal solution is studied as are the others from the original alkaloidal precipitate. The volatile oils, if in any appreciable amount, should have their specific gravity, odor, optical rotation, solubilities in alcohols of various strengths, and limits of boiling temperature determined by the methods described in Chapter II.

Attempts should now be made to separate definite chemical bodies from the residues from each of the various fraction solvents, and in no place can skillfully managed fractional crystallization be made to serve to better purpose than here, and indeed it often offers the only means of attacking the problem. A substance must be obtained with a fixed boiling- or melting-point after repeated distillations or crystallizations before it can be assumed to be a chemical unit, and this is

the goal toward which the analyst is striving. Often, however, this ideal is not realized, and the best that can be had in the present state of our knowledge is an amorphous, often resinous mass, with no very sharply defined chemical properties. This must not be construed by the beginner, however, as meaning that the said body may not possess very active physiological properties.

Short Method

The foregoing plan of separation is the one recommended for the investigation of any new or unstudied drug. In the case of the known and commonly used ones, the determination of one or more bodies known to be the active therapeutic agents may be all that is required, and as this will more frequently be an assay it may be more quickly accomplished by the methods described in Chapter X. In other cases the great expenditure of time may necessitate a shorter procedure, and here the following short process may be substituted.

. Extract with alcohols as usual. Evaporate or distill in a partial vacuum to remove camphoraceous bodies, volatile oils, volatile acids and, from alkaline solutions, volatile alkaloids.

Add water if necessary, filter and wash through a thick filter, using some inert absorbent powder if necessary, and dry the residue of fats, waxes, phlobaphenes, resins, etc.

Acidify the filtrate with hydrochloric acid, saturate with sodium chloride, and extract with ether containing about 20% of alcohol, or with acetic ether for organic acids, glucosides, colors, some alkaloids, portions of the tannins, etc.

Make the aqueous solution alkaline with ammonia and extract with a mixture of four parts ether and one part chloroform or with chloroform alone for alkaloids, possibly also some neutral bodies which were soluble in chloroform but insoluble in ether.

Neutralize the aqueous solution or render faintly acid with acetic acid, evaporate to dryness, and extract the dry salty mass with acetone, or sometimes strong alcohol.

Again dissolve the residue in water, where alcohol was not used, and examine for sugars, gums, extractives, etc. Digest the residue with hydrochloric acid and potassium chlorate to destroy organic matters, and examine for inorganic matters if necessary.

This short scheme will also be often of service in the examination of medicines generally, other than crude drugs, as where the subsequent crystallizations are successfully performed, the majority of organic synthetic medicines, alkaloids, and commonly used neutral bodies fall into well-defined groups here. Indeed in ordinary routine examinations it will generally furnish all the information desired, especially if after separating the various bodies their precipitations with normal and basic lead acetate and alkaloidal reagents is determined, when the tables given (see Table I), can be used as well as with the previously described long method.

DETERMINATION OF THE CHEMICAL PROPERTIES OF SEPARATED BODIES

Besides observing the crystalline form, melting-point or boiling-point, color and precipitation tests, solubilities and perhaps also the results of an elementary analysis for fixing the identity of separated bodies,

where they are known, and these constants already
recorded for them, additional studies will also be often
desirable; either for further confirmation of their
identity or, as in the case of possibly new or poorly
described bodies, for obtaining further information as
to their structure and other chemical properties.

Fats. Any separated fats, when in an important
quantity, should have the following data determined
for them when possible.

First, their melting-point.

Second, their saponification number, which is deter-
mined by boiling a known weight of the fat with a
measured excess of normal alcoholic solution of potas-
sium hydroxide until completely saponified, diluting
somewhat with water and titrating back with normal
acid, using phenolphthalein as an indicator. The
calculated number of milligrams of KOH found to
combine with 1 gram of the fat is the saponification
number.

Third, their iodine number, which is determined
by digesting a weighed amount of the fat, first dissolved
in chloroform, with an excess of alcoholic solution of
iodine containing mercuric chloride until no more
iodine is absorbed, and titrating with sodium thiosul-
phate solution to find the amount absorbed by 1 gram.

Fourth, the proportion of insoluble fatty acids, which
may be obtained by adding an excess of mineral acid
to the titrated liquid from the determination of the
saponification number, warming until the melted fat
acids form a clear layer on top of the liquid, allowing
to cool, and filtering off and washing with cold water
the solid cake of acids, after which they are dried for
weight.

Fifth, their melting-point: this latter being more

nearly a fixed constant for single natural fat acids than is the melting-point of the fat itself. Other data, such as the heat or bromination, refractive index, acetylization number, etc., may also often be of use.

Waxes. These are in general combinations of fatty acids with alcohols of higher molecular weight than glycerol, and unlike the latter generally insoluble in water, so the methods for their separation from the waxy acids after saponification are somewhat different from those employed in the case of the fats.

In most other respects the methods for the examination of the two classes of bodies and the constants to be determined are essentially the same in each case.

The saponification numbers, etc., of some of the common waxes and fats are given in Table VI.

Resins. Resins can often be separated by treatment with different solvents. They are then saponified by boiling, often for a considerable time, with alcoholic KOH and their saponification number determined in the alkaline filtrate as in the case of fats, the unsaponifiable matter being washed and weighed. The solution is now again made strongly alkaline with KOH, an amount corresponding to 75% of water added, and the liquid extracted with ether or other suitable solvent which will dissolve the resin alcohols. The residual aqueous solution is now made acid with sulphuric acid and again extracted with ether or other solvent, which will remove the resin acids. This separation is sometimes, however, far from satisfactory. The free resin acids are also often determined by dissolving the resin in a neutral solvent, adding phenolphthalein, and titrating directly with standard alkali.

According to Tschirch, resins, freed from their contained volatile oils by steam distillation if necessary,

may consist of : I. Resens, which are insoluble in potash solution; II. True resins, which are compounds of resin acids with resin alcohols; III. Free resin acids or their anhydrides; or IV. Any mixture of these. Resin alcohols are by him designated as resinols when they are colorless and give no ink reaction with ferric chloride, and as resinotannols when they are colored and give the ink reaction. Common rosin is an example of the third class, being supposed to be the anhydride of abietic acid. The resin acids belong either to the benzoic acid or cinnamic acid class. The common chemical and physical properties of these separated bodies should be determined after their isolation. The chemical constants for some common resins are given in Table X.

Glucosides. These bodies are quite generally distributed in the organic kingdom. Many are practically physiologically inert and occur in commonly used foodstuffs, while some, with the exception of the alkaloids and a few volatile oils, are among the most physiologically active bodies among plant constituents. It is often a difficult matter to separate them in a definite crystalline condition, although their products of hydrolysis, other than the always present sugars, are more readily handled. So besides determining the melting-points, color reactions, etc., of the bodies themselves, a study of the bodies split off by heating with acids, should always be made. A large number of the tannins, plant acids, and coloring matters, etc., existing in plants belong to this class.

For determining the glucosidal nature of a body, a small portion is first boiled with Fehling's solution and if by this treatment no reduction of copper occurs, another portion is heated for some time in a closed strong bottle with from 2 to 10% of hydrochloric acid.

Still another method advises heating the substance with hydrochloric acid in a sealed glass tube in a boiling water-bath for some hours. The acid is now neutralized by soda and a portion of the neutral liquid again tested with Fehling's solution, and phenylhydrazine, sodium acetate and acetic acid, for reducing sugars, which if present show the body to be glucosidal in nature. The osazones formed with phenylhydrazine under proper conditions have definite melting-points for the different sugars. The main portion of the liquid is now slightly acidified with a mineral acid, and completely extracted by shaking out with ether or other suitable immiscible solvent, and on the evaporation of this latter the resulting residue is purified and its properties determined.

Plants, of course, contain neutral bodies soluble in organic solvents other than glucosides, although the latter may be said to predominate.

Tannins. A small portion of the aqueous solution of the acetic ether extract is treated with a drop of dilute ferric chloride or of iron alum solution, and another is shaken with a portion of moist rawhide powder or gelatin, when a blue-black or greenish-black color in the first instance or an absorption of the body by the hide powder in the second, is indicative of tannins. A portion of the tannin is heated to about 200° C., for an hour with 5 c.c. of glycerin, the product diluted somewhat with water, slightly acidified, and extracted with ether in a separator. All tannins will by this treatment yield either pyrogallol, giving a blue-black color with dilute iron alum solution, catechol, giving a green-black color with the same reagent, or frequently phloroglucinol, which gives no reaction with iron, but a violet to brown color and a white pre-

cipitate with calcium hydroxide and bromine water respectively.

Another portion is heated for about an hour with 1% hydrochloric acid, preferably in a sealed glass tube, in a boiling water-bath. It is then cooled, filtered, and the filtrate extracted with ether which is allowed to evaporate. The residual aqueous liquid is neutralized with sodium or potassium hydroxide, precipitated with a slight excess of basic lead acetate solution and after filtering, the excess of lead removed by hydrogen sulphide. We have now separated our tannin into first, an insoluble precipitated from boiling with the acid; second, a portion shaken out with ether from the acid solution and, third, a clear aqueous filtrate. The clear filtrate is tested with Fehling's solution, when a reduction will indicate that we are dealing with a glucosidal tannin. The ether extract may contain gallic acid, which will give a red color with potassium cyanide solution, and the insoluble residue may consist of phlobaphenes, which are soluble in cold alcohol, ellagic acid, the source of the leather "bloom" in the tanning industry, which is soluble in hot alcohol, or only of lead chloride, which is dissolved by a sufficient quantity of hot water: further, ferric chloride gives a blue color with gallic acid, a greenish to black one with ellagic acid, and no reaction with pure phlobaphenes. Nitric acid gives a crimson color with ellagic acid but little reaction with others. Phlobaphenes are easily soluble in dilute alkalies.

Among those tannins which by this treatment yield gallic and ellagic acids but *no* phlobaphenes, are those of nutgalls, sumac, pomegranate, etc. Among those yielding both gallic and ellagic acids *and* phlobaphenes are those of quercus alba, chestnut, etc., and among

those which are changed practically entirely into phlobaphenes are those of catechu, kino, krameria, quebracho, horse chestnut, etc. The phlobaphenes, both natural and those formed by the above treatment, are chemically to a greater or lesser extent the anhydrides of the tannins. They may be studied by fusing them with four or five parts of potassium hydroxide, dissolving the mass in water, supersaturating with sulphuric acid, and extracting with ether. The residue from the evaporation of the ether will probably contain protocatechuic acid, and ether phloroglucinol, with no sugar in the aqueous residue, or fatty acids and some sugar in that residue, i.e., some phlobaphenes, like their parent tannins, are glucosides while some are not. Among the glucosidal ones are those of male fern, coffee, cinchona, etc., and among those which yield phloroglucinol and no sugar are those of catechu, kino, krameria, etc. In determining which of these reactions has taken place the following reactions may also be used. Lead acetate gives precipitates with most of the fatty acids, none with phloroglucinol, but a bluish-green one changing to red on the addition of caustic potash with protocatechuic acid. Fehling's solution is reduced by phloroglucinol but not by protocatechuic acid, and since phloroglucinol exists in the non-glucosidal tannins, care must be exercised to prevent confusion.

Volatile Oils. With the small quantity of volatile oil which it is generally possible to obtain from non-aromatic drugs, the appearance, odor, and solubilities in alcohols of various strengths are all that one is able to observe. When a few cubic centimeters (two or more) are obtainable, the approximate determinations of specific gravity, optical activity, etc., are possible.

The specific gravity of small quantities of the oil may be determined by sucking it up into a thin light tared capillary tube, constricted at one end and having a mark near the other, drying the outside of the tube and weighing it filled to the mark with the oil at a definite temperature. The weight of the oil divided by that of a like volume of water in the tube gives the specific gravity. With care this may thus be obtained accurately to the second decimal place. The optical rotation, either to the right or left, is often an important determination. It may be determined by any of the ordinary forms of polarimeters, but as in the case of the specific gravity determination, the smallness of the sample generally necessitates the employment of an especially narrow observation tube which can be readily extemporized, or the oil may be examined in alcoholic solution. The extent of the right or left rotation when present should be determined as accurately as possible in a 100 mm. tube.

The solubility of the oil in diluted alcohol is another determination which often furnishes valuable information. For this purpose a definite small amount of the oil, which may conveniently be taken from the small specific gravity tube, is rinsed into a small flask with exactly twenty times its amount by volume of absolute alcohol, or in the absence of this with strong alcohol the exact strength of which is known. Water is now added drop by drop from a burette to the alcoholic solution, with constant shaking, until the first permanent turbidity remains, when the amount of water used enables one to calculate the strength and quantity of the diluted alcohol.

Many of the so-called steroptens, consisting mostly of camphoraceous bodies, etc., may separate themselves

on strongly chilling the oil and may be then removed.

The chief advantages of these three tests are that they in no way injure the oils for future reference and that the determinations may, with care, be made on but little over 1 c.c. of the sample. The temperature at which the oil begins to boil may also be determined with sufficient accuracy by using the capillary tube as described in Chapter V.

When larger quantities of the oils are available, the constants may of course be determined more accurately by ordinary methods and some idea of the chemical constitution of the bodies may also be had, although with bodies which may contain such a wide variety of substances as aliphatic and aromatic hydrocarbons, alcohols, acids, esters, aldehyds, ketones, phenols, lactones, and various nitrogen and sulphur compounds, any definite plan of procedure is difficult to outline. Fractional distillation through a good distilling tube will sometimes furnish information, but in many cases a satisfactory separation of the constituents of a volatile oil by this means is not to be had. *Phenols* may often be approximately removed by shaking the oil with a small quantity of 5% potassium hydroxide and afterward precipitating the phenols from the neutral of faintly acid solution with bromine water.

Many *aldehyds* and *ketones* may be removed by shaking the oil with a strong solution of sodium bisulphide and afterward liberated by sulphuric acid. *Esters* may now be saponified by boiling for some time under a reflux condenser with KOH solution, the combined *alcohols* distilled off with steam, and the *ester acids* liberated from their potassium salts by a slight excess of some mineral acid. *Alcohols* when known may be determined by heating a portion of the oil under a

reflux condenser, with a like volume of acetic anhydride and some *perfectly dry* sodium acetate, afterward determining the saponification number and deducting that previously obtained on the non-acetylized sample. The saponification number is here increased by the formation of acetic acid from acetic anhydride and hydroxyl groups of the alcohols present. Some *hydrocarbons*, etc., when present in considerable quantities, may separate on standing from the alkaline solution from the last saponification and may be separated and further purified, but as they are all to a certain extent soluble in water, small quantities may escape detection. The more common constants of volatile oils are shown in Table VII.

Plant Acids and Colors. These are so diverse in nature that the methods for their examination will from necessity vary considerably. Acids are generally best separated in the form of their silver, lead or barium salts and purified by crystallization from water or organic solvents, after which the acids may be liberated by hydrochloric acid, washed, and their chemical and physical constants determined. Colors should have the absorption spectra measured and recorded, not only in the natural free state but also in acid and alkaline solutions. As both the acids and colors are often of a glucosidal nature, hydrolysis with dilute hydrochloric acid as in the case of the tannins will often furnish valuable information. In the case of the acids, the determination of the basicity is of considerable importance.

Alkaloids. These are without doubt the most important class of plant constituents from the pharmacological standpoint. What the drug analyst will care most to know of the majority of them will be their

color reactions, precipitants, and the melting-points of both the free bases, their principal salts and double compounds, all of which serve for identification purposes.

Studies of their decomposition reactions and products are of less value from the purely analytical standpoint than are those of the glucosides, tannins, etc., because most of the alkaloids fortunately have well-marked chemical and physical and especially physiological properties.

WATER EXTRACT

The residue from the alcohol extraction is digested with frequent agitation with water, or with water containing about 5% of alcohol or from 5 to 20% of glycerin for the temporary preservation of the solution, for a day or more at a temperature of from 30 to 50° C., the watery extract strained off and the drug residue allowed to digest again with a fresh portion of menstruum for several hours. The mixed liquids may contain gums, sugars, soluble starch, dextrin, various proteid bodies, pectous substances, etc., and possible saponin bodies and ferments.

The last are about the only bodies which are of much interest to the drug student. If saponins are present in any appreciable amount, the liquid, even when quite dilute, will show a strong permanent foam on shaking. If this be present in sufficient amount to warrant suspicion of the presence of these bodies, which would also probably have been found in smaller amounts in the alcoholic extract, an aliquot portion of the aqueous liquid is evaporated somewhat, treated first with normal and then with basic lead acetate and the resulting precipitates treated as directed under the water soluble portion of the alcoholic extract. The

neutral lead acetate precipitate may contain substances like quillajic acid from soap bark, and the basic lead acetate precipitate those similar to true quillaja saponin, sapotoxin, etc. Either solution will foam strongly on shaking, a phenomenon which might also be due in a lesser degree to substances like gum, etc., and will have a characteristic acrid taste, which is not possessed by the other bodies. Further, these bodies are apt to give with strong sulphuric acid characteristic color reactions, red in the case of bodies like quillajic acid and yellowish-red, changing to red, dark red, violet and finally brownish on warming, in the case of sapotoxin. Similar color reactions are also given by the polygalic acid and senegin from senega root, bodies closely related to the above. For the quantitative determination of these bodies, the neutralized liquids resulting from the decomposition of the lead precipitates may be evaporated at a low temperature, the saponin bodies carefully extracted with 50 or preferably with 75% alcohol, and the alcoholic solutions evaporated for weight.

Ferments. These are as a rule not present in dried drugs to the extent which they are in the fresh material. For their determination there are a number of methods in vogue, the best one depending as usual on the particular circumstances.

Generally they are best precipitated from an aliquot portion of the water extract by an excess of strong alcohol, corresponding to 75 or 80% of the mixture, and further purified by similar reprecipitation by alcohol, or as may frequently be done, by saturating the aqueous solution of the original precipitate with some neutral salt as, e.g., magnesium sulphate or sodium phosphate. Some ferments are precipitated by calcium phosphate,

the solution being first acidified by phosphoric acid and then the correct amount or a slight excess of lime solution added. The complete freeing of these ferment precipitates from mineral salts is a difficult process, although dialysis will sometimes accomplish it if a slight preservative such as 5% of alcohol be added to prevent decomposition.

The action of these separated ferments is tested by placing a small quantity of the substance in weak solutions of albumen, cane sugar, starch, salicin or other glucosides, and observing whether these latter are to any extent changed to peptones (giving a red voilet color with very dilute Fehling's solution) or to reducing sugars (by their action with boiling Fehling's solution or the formation of osazones with phenylhydrazine acetate) within a few hours.

Reducing Sugars. If shown to be present by Fehling's solution, these may be determined by titrating an aliquot portion of the original water extract against a measured amount of that reagent, adding the solution from a burette to the diluted Fehling's solution which is kept boiling in a flask for two minutes after each addition; after one of these latter the blue color is seen to have entirely vanished and the copper to have been all precipitated.   Each c.c. is equivalent to 0.005 gram of glucose.

In the absence of other optically active bodies, the reducing sugars may be conveniently determined by the polariscope in the clear white filtrate from the basic lead acetate precipitate, an aliquot portion of which is made up to a definite measure before polarization.

Cane-sugar, with any *soluble starch*, is determined by heating 50 c.c. of the water extract mixed with 5 c.c.

of strong hydrochloric acid to 70° C., in a water-bath and holding the mixture at this temperature for five minutes, after which it is neutralized, made up to 100 c.c. with water, and titrated with Fehling's solution as before, making due allowance for any reducing sugars which may have been previously found present.

These sugars are also conveniently estimated by the polariscope. The main portion, or all of the *starch*, is determined in a similar manner, by heating about 2 g. of the powdered drug residue in a tightly closed strong bottle containing 2% of hydrochloric acid, in a boiling water-bath for two hours, neutralizing and titrating with Fehling's solution as before. The sugar found is to be multiplied by 0.95 for starch.

Soluble Proteids are accurately enough determined by digesting an aliquot portion of the water extract with boiling strong sulphuric acid until the water is all evaporated and the acid solution colorless, and estimating the ammonia formed as in the regular Kjeldahl method for nitrogen. The nitrogen found multiplied by 6.25 is the crude soluble protein.

Total Crude Protein is determined in a fresh lot of the dry material (0.50 to 1.00 g.) by the regular Kjeldahl method, multiplying the nitrogen found by 6.25 as above.

OTHER SCHEMES OF PLANT ANALYSIS

Of the older schemes, those of Dragendorff and Parsons previously referred to have been used with more or less modification for the major portion of all the older drug analyses. They are here reproduced in short form for reference.

DRAGENDORFF'S SCHEME

1. Determine moisture and ash.
2. Extract the dry drug with light petroleum ether and allow the extract to evaporate in a dry air current desiccator.

   A. Volatile—volatile oils, volatile acids, volatile alkaloid.

   B. Soluble in acid waters—alkaloids.

   C. Insoluble—fats, waxes, chlorophyll, etc.

3. Extract the residue from the above with stronger ether; evaporate.

   A. Soluble in water—gallic acid, alkaloids, glucosides.

   B. Soluble in alcohol—benzoic acid, salicylic acid, etc.

   C. Soluble in alkailes—resins, etc.

4. Extract the residue from the above with absolute alcohol.

   A. Soluble in water—alkaloids, glucosides, tannins.

   B. Soluble in 2% ammonia—phlobaphenes.

   The water soluble portions of 2, 3, and 4 are united and extracted in a separator in *acid solution* with petroleum ether (benzin), coal-tar benzene and chloroform. The liquid is again extracted with petroleum ether to remove dissolved portions of the used solvents, made *alkaline* with ammonia, and again extracted in succession with petroleum ether, benzene, chloroform, and amyl alcohol. Various substances are left in the residues from the evaporation of these several solvents, mostly alkaloids and glucosides, which are then further examined.

5. Extract the residue from the absolute alcohol extraction with water.

  A. Pectous substances, albumenoids, inulin, dextrin, sugars, acids, saponins, etc.

6. Extract the residue from the above with alkaline water (hot).

  A. Albumenous substances, pectous compounds, etc.

7. Extract the residue from the above with boiling acid water.

  A. Starch and ash constituents.

8. Insoluble residue.

  A. Lignin, cellulose, ash, etc.

PARSONS' SCHEME

 This includes:

1. The determination of moisture.
2. Ash.
3. Total nitrogen as a check on later determinations.
4. Total benzene or chloroform extract.

  A. Volatile—volatile oils, camphors, etc.

  B. Soluble in water—alkaloids, glucosides, acids, etc.

  C. Soluble in dilute acid—alkaloids and glucosides.

  D. Soluble in 80% alcohol—resins.

  E. Insoluble—waxes, fats, oils, etc.

5. Total 80% alcohol extract.

  A. Soluble in absolute water.

   1. Soluble in water.

     a. Precipitated by basic lead acetate—tannins, glucosides, organic acids, extractives, colors, etc.

     b. Not precipitated by basic lead acetate—alkaloid and glucosides.

2. Insoluble in water.
   a. Soluble in dilute acid—alkaloids, glucosides.
   b. Soluble in dilute ammonia—acid resins, colors.
   c. Insoluble—neutral resins, colors, etc.

B. Insoluble in absolute alcohol.
   1. Soluble in water.
      a. Precipitated by basic lead acetate —colors, extractives, acids, etc.
      b. Not precipitated by basic lead acetate—alkaloids, glucosides, glucose, sucrose, extractives, etc.
   2. Insoluble in water.
      a. Soluble in dilute acid—alkaloids, glucosides.
      b. Insoluble in acids—resins, extractives, colors.

6. Total cold water extracts, gums, pectous substances, dextrines, soluble starches, albumens, colors, soluble ash constituents, sugars.

7. Total portion soluble in boiling dilute hydrochloric acid, starches, sucrose (inverted), albumens, etc.

8. Total 1% KOH solution extract, albumens, pectin compounds, humus, etc.

9. Insoluble residue.   Cellulose, lignin, ash, etc.

CHAPTER VII

ANALYSIS OF MEDICINES GENERALLY

From the foregoing chapters some idea will also have been obtained of the general methods to be followed in the analysis of unknown medicinal mixtures. The volatile matters are first separated, vegetable drug extracts identified and their approximate quantity estimated by separating and determining one or more characteristic proximate principles which are known to exist in them in more or less definite proportions; mineral matters by the usual inorganic analytical methods; organic synthetics by the use of various solvents and the methods common to organic chemistry, generally, as in the case of the proximate plant constituents; and organized crude drug powders by the methods of microscopical drug analysis, described in Chapters VIII and IX.

Attention may well be again called, however, to the importance of a thorough familiarity with the sensible properties of the more common pharmaceutical preparations of the various drugs, for often a characteristic appearance, odor, or taste, will quickly furnish more information to the experienced observer than will hours of patient work do for the novice in this work.

While, as before stated, the number of possibly present drugs or synthetics may be almost legion, most of the unusual bodies are apt to be unimportant from the practical standpoint, and the nature and

133

merits of the mixture may generally be safely judged from its better known and more useful constituents.

The methods to be pursued in any individual case will depend somewhat on the particular form in which the medicine is found, whether as a solution or other liquid, ointment or powder. Tablets, capsules and pills are essentially the same as powders in their nature except that the latter especially are filled with a mass of extractives, etc., and are more often coated with a layer which is apt to be gelatin, sugar or chocolate, except in certain cases where the pills are desired to be insoluble, in the stomach, when they may be coated with keratin, or salol, etc.

PRELIMINARY EXAMINATION

If the mixture is a liquid, take the specific gravity with a hydrometer or pycnometer. If this be less than unity, it is generally an indication, except in the case of oily mixtures, that alcohol is present. A few drops are then evaporated on a piece of platinum foil at a gentle heat for the formation of any solid residue; if in doubt, a somewhat larger quantity may be evaporated in a small porcelain dish. If a residue is present, or in the case of powders, it is carefully ignited over a small flame for any residue of mineral matters. The odor during this ignition should be carefully observed for any characteristic fumes. An odor of burning hair is strong indication of nitrogenous matter, probably of animal origin (ferments, etc.). A portion of the dry residue is tested for its solubility in water, and another in alcohol, allowing the clear portions of the solvent to evaporate on a glass

slide, in each case for the purpose of observing the character of the residue, especially the presence or absence of crystals.

A portion of the aqueous solution is also tested with normal lead acetate, and after filtering off the precipitate if any, with basic lead acetate. These reagents will always give dense precipitates in the case of vegetable extracts and often also in the case of other bodies, so an approximate idea of the relative amounts of these precipitates is desirable here. Another small portion of the liquid is made alkaline with ammonia, shaken with ether in a small vial or test tube, the ether allowed to completely separate, removed by means of a pipette, allowed to evaporate, the residue taken up with 1% acid and tested with a drop of potassio-mercuric iodide, or other suitable reagent when any cloudiness and especially any dense precipitate will indicate the presence of alkaloids. A portion of the dried residue is also ignited carefully on a borax bead in a colorless flame when a green boric acid flame or spectrum will indicate glycerin, although a more certain method is to mix the dry residue with borax, cover it slightly with alcohol and ignite the latter when a green mantle to the flame, especially when it is repeatedly extinguished and relighted, will show the presence of the body.

Another small portion of the original liquid, especially if it has any sweet taste, is heated in a small test tube with a few drops of hydrochloric acid, neutralized, and tested for sugar with Fehling's solution. It must be remembered here, however, that other substances than added cane sugar may cause a reduction of the copper. A drop of ferric chloride solution will show a dark bluish-black, or greenish-black coloration

when tannins are present and will give various violet or reddish-violet colorations with phenols, cresols, salicylic acid derivatives, etc. Iodine solution may also show the presence of starch in various vegetable infusions.

Alcohol will generally be apparent from its odor except where this is masked by other substances, but if necessary it may be tested for by distilling a few drops carefully from one test tube to another by means of a perforated cork and bent-glass tube, and warming the clear distillate with a little sodium hydroxide, potassium iodide and iodine, when on cooling a pale yellow precipitate of iodoform will separate. Other bodies such as aldehyds, acetone and other alcohols may of course give this reaction. Other volatile substances will generally be apparent from their odor. In the case of salves or oily liquids, the fatty substance is to be dissolved by petroleum ether, and the fat-free residue treated as above.

In a great majority of cases the experienced drug analyst will not need to follow out the above preliminary examinations, as his acquaintance with the different types of medicines will at once enable him to exclude some of the substances sought or to detect others by more ready means; but, in any case, some general idea of the make up of the mixture should be obtained in some way before attempting to formulate a method for attacking the problem more carefully.

SYSTEMATIC ANALYSIS

LIQUIDS

Total Solid Matters.   Evaporate a few grams or, for convenience in future reckoning, cubic centimeters, in a tared broad dish, dry to constant weight at about 90° C., and weigh.   Where the amount of available sample is small or for other reasons the following procedure is often preferable.

Distill a measured portion of the liquid to incipient dryness in a tared flask resting in a water-bath, using as low a temperature and as high a vacuum as possible. For this purpose the apparatus shown in Fig. 4 answers well.   In case the liquid is distinctly acid or alkaline in reaction, it is previously titrated with standard acid or alkali as the case may require and the result noted.   Care must be also used not to heat longer than is required to expel the free liquid.   The flask is then wiped clean and dry on the outside, and dried in the water-bath oven at about 80° C., or preferably in a desiccator over sulphuric acid until the weight remains constant, and weighed; correct for any soda or acid added.

The *volatile matters* are all contained in the distillate and are to be examined by Table I, 1.   The weighed residue in the flask is treated with a quantity of 75% alcohol and heated in the hot water bath to about 40 or 50° C., thoroughly working up the residue with the liquid by means of a stout glass rod.   After settling, the clear liquid is carefully decanted and the residue repeatedly extracted with warm 75% alcohol until, in the case of thick liquids containing much vegetable matter, a volume equal at least to the original volume

of the liquid taken has been used. The flask is then again dried and weighed and from the weight of the residue the *portion soluble in* 75% *alcohol is calculated.*

In the case of liquids known to be strongly alcoholic this treatment may of course be dispensed with, and where an insoluble residue does not settle out from the 75% alcohol used the operation may terminate there.

The 75% alcohol solution is now again evaporated in the vacuum distilling flask as before and the residue taken up with repeated portions of water heated to about 60 or 80° C., as in the case of the alcohol extraction, until a drop when allowed to evaporate on a glass slide leaves no appreciable residue, filtered hot, the solution again evaporated somewhat if necessary on account of inconvenient bulk, and allowed to stand for some time in a cool place. Any deposit which may form is filtered off and examined. If, of complex nature, it is examined along with the alcoholic *residue insoluble in water* by Table I, 2.

If much vegetable matter is present and especially if the sample does not require to be also used for the subsequent mineral determinations, the aqueous solution is now treated with the lead salts. In the absence of these conditions it may be extracted at once by the immiscible solvents first in acid and finally in alkaline solution, the solution being first evaporated at a low heat to a convenient volume and possibly also saturated with salt to secure better separation. In the use of the tables it really does not matter much which method is pursued, as the reaction of the various bodies to normal and basic lead acetate may be determined with other tests after their isolation, but with certain glucosidal and other neutral bodies from plant extracts,

isolation without the use of the lead salts may be more difficult.

To the clear warmed filtrate a slight excess of 25% normal lead acetate solution is now added, the whole allowed to stand for some time, filtered, the precipitate washed, decomposed and the lead free filtrate extracted with solvents as directed in page 111, and the substances in the residue sought for in Table I, 3, 1. Basic lead acetate is similarly added to the filtrate and washings from the above together with enough dry litharge to convert any excess of the normal salt into the basic one, allowed to stand in a warm place, filtered, the precipitate decomposed and the lead free filtrate extracted as described in III, page 111, the substances in the residue sought in Table I, 3, 2.

As traces of alkaloids may be retained by this precipitate, it is well where these have been found by the preliminary examination, to wash the lead carbonate resulting from decomposing this precipitate with 50% alcohol, and to add the residue resulting from the evaporation of the latter to the main acidified solution, from which alkaloids are to be precipitated. The filtrate from the basic lead acetate precipitate is slightly acidified, freed from lead by hydrogen sulphide, filtered, the lead sulphide on the filter washed somewhat with 50% alcohol, and the filtrate and washings evaporated to a relatively small volume in the vacuum apparatus, using again a very moderate heat; or, if alkaloids have previously been shown to be absent by the preliminary examination, nearly to dryness.

Where alkaloids are present or not known to be absent, the liquid is treated drop by drop with potassio mercuric iodide solution, phosphomolybdic acid or other suitable alkaloidal reagent, filtered and the precipitate

washed slightly with water.   The precipitate is then decomposed by stannous chloride and some weak sodium hydroxide or with NaOH alone according to the reagent originally employed, made slightly acid, filtered, the filtrate extracted with immiscible solvents as directed in IV, page 112, and the alkaloids sought for in Table I, 3, 3.   The final filtrate from the alkaloidal precipitate, or where no alkaloids were present, from the basic lead acetate precipitate is free from the excess of precipitant, carefully neutralized if further concentration is desired, and extracted in succession with the solvents mentioned in IV, page 113, the substances in the various residues being sought for in Table I, 3, 4.

We have now separated the alcoholic solution of our medicine, like our alcohol plant extract in page 109, into about 25 fractions, and in one or several of these active or other characteristic bodies may be found. The residue left by the last extraction by 75% alcohol, as well as the residue from the evaporation of this solvent itself, may contain sugars and other bodies which are less readily soluble in alcohol and other organic solvents than in water, and where a water-soluble portion is to be examined, this may often be more conveniently added to it.

Careful search must now be made for characteristic bodies in these several residues, and for this purpose fractional crystallization offers generally the most promising results.   It must not be forgotten, however, that many important bodies have thus far not been obtained in a pure crystalline form, and for this reason it is never safe to slight the examination of a persistently amorphous mass.   Many bodies such as plant acids,

alkaloids and others can generally be best separated in the form of salts or other definite compounds, which crystallize better than the free compounds. In the case of alkaloids, not only the chemical and physical properties of the free base, but also those of the common salts, and especially their compounds with such precipitants as gold and platinic chloride, iodine, picric acid, etc., should be found. The latter compounds may often be caused to crystallize well by dissolving the precipitate formed in the slightly acid aqueous solution by the several reagents, in a little alcohol and allowing the solution to slowly evaporate. The melting points of these crystallized compounds are much more constant than those of the more common salts.

Where the original mixture is known to have some pronounced physiological effect on animals, the residue in which this effect is found to reside will of course, contain the chief constituent sought.

————

Where few or no plant extracts are found to be present by the preliminary examination, where interfering inorganic salts such as chlorides, bromides, iodides, sulphates or phosphates exist, or where the residue from the extraction with organic solvents has also to be used for a subsequent inorganic analysis, the precipitations by lead salts and alkaloidal reagents are generally best omitted as before stated, and the liquid after the separation and washing of the water-insoluble matters, is concentrated at a low temperature, acidified by a few drops of dilute sulphuric acid, saturated with *pure* sodium chloride or sodium sulphate, where these will not interfere with subsequent inorganic determinations, and extracted with ether containing

a little alcohol, as directed in Chapter VI, page 115, for acids, colors, glucosides, traces of tannins and some alkaloids. The solution is then made alkaline with ammonia and extracted with a mixture of ether four parts, and chloroform one part, for alkaloids. The aqueous residue is then neutralized, evaporated to dryness and the salty mass extracted with acetone or strong alcohol.

In the residues from these organic solvents small portions of saline impurities from the salts used may be found and must be allowed for, and in the final saline residue sugars and other similarly deporting bodies may of course be found. The mass is finally digested with hydrochloric acid with the addition of nitric acid or of potassium chlorate to destroy organic matters if necessary, and subjected to the usual inorganic analytical routine. The organic medicinal bodies extracted by the organic solvents are examined for their solubilities in benzene, chloroform, and acetic ether, and for their precipitation reactions with neutral and basic lead acetate, after which they may be sought for in the tables.

———

The residue insoluble in alcohol in the original distilling flask, if any, may consist of plant extractives, gums, sugars, possibly unorganized animal products, as e.g., ferments, and of any inorganic mineral matters insoluble in alcohol. It is dissolved in water and added to the final water solution.

The quantity of any nitrogenous animal substances present is generally to be calculated from the total nitrogen content. Naturally most of these (generally unorganized ferments) cannot be present where the

original solvent was strong alcohol or where it contained mercuric, cupric or other inorganic salts which precipitate these substances. As few of these admit of satisfactory systematic separation from each other, they are generally to be qualitatively tested for after physiological methods in fresh portions of materials, by digesting them at about blood-heat in acid and alkaline solution, with albumens, and cooked starch and observing the results.

Glycerin when present in a mixture, is a strong interfering factor, especially with the separation of alkaloidal precipitates, as it is soluble both in water and alcohol, practically non-volatile, and so cannot be separated primarily. When the amount is not excessive, the solution may be extracted directly as above described with immiscible solvents, but when present in any considerable amount special methods will frequently have to be devised. Sometimes it may be directly precipitated by a large excess of ether and after standing for a time the ethereal solution containing most of the other bodies sought filtered off and the ether recovered. Its quantity when in nearly pure aqueous solution may be sufficiently accurately calculated from the specific gravity of the mixture (see Table VIII). When interfering bodies are present it may be precipitated with ether as above, or the entire mass of liquid may be treated with *dry* sodium sulphate until all is absorbed by the salt, after which the mass is extracted with acetone which dissolves the glycerin with perhaps portions of some other bodies. Small amounts of glycerin may be determined by making the liquid strongly alkaline with potassium hydroxide, adding 5% potassium permanganate solution until the mixture is of a purple or black color, heating to boiling, filtering,

decolorizing if necessary with sulphurous acid, precipitating the oxalic acid formed by oxidation of the glycerin with calcium chloride in acetic acid solution, and titrating the calcium oxalate so formed with tenth normal potassium permanganate, each cc. of which is equivalent to 0.0047 g. glycerin.

When acetic acid is present in the menstruum, it will as a rule have been titrated with NaOH solution before the original evaporation of distillation and the resulting sodium acetate carried through to the final residue. In practically all other cases the menstruum will have consisted simply of water, or of water containing varying portions of alcohol, both of which will have been distilled off and recovered with the volatile matters. Alcohol, in the absence of other substances than water in the distillate, may be calculated from the specific gravity of the distillate, by reference to Table V; where other substances are present in appreciable quantity they must be first separated. In case no distillation has been performed, the alcohol may be calculated by carefully taking the specific gravity of the original mixture, evaporating an accurately measured quantity of it to about one-fourth its original volume or less, again making up to the original volume taken with water and taking the specific gravity of this latter solution. The difference between the two specific gravities, subtracted from one, will give the specific gravity of a liquid having the same alcoholic strength as the mixture. Methyl alcohol when present may for all practical purposes be calculated from the same tables as is ethyl alcohol, as the difference in their specific gravities is slight. Acetone and ether may occasionally be found in mixtures for external application and will generally be recognized by their odor.

They may be separated from water, alcohol and each other by careful fractional distillation through a high distilling tube.

OTHER VOLATILE MATTERS

The bodies volatilized and found here will depend in many cases on the reaction of the original liquid when distilled. In the foregoing paragraph we have assumed the absence of all volatile matters except such as may have been used as a menstruum. Besides these it will be evident that numerous medicinal bodies may be present. The odor of the distillate is to be carefully observed, as it will give the characteristic odors of any or all of the volatile substances. Its reaction is to be tested with delicate litmus paper, or preferably phenolphthalein, its specific gravity taken and if this indicates the presence of much alcohol the whole is diluted with water until the alcoholic strength is not over 20 or 25%. It is then saturated with salt and completely extracted with light petroleum ether (boiling-point 30 to 50° C.). After separation an aliquot portion of the petroleum ether is allowed to stand in a dry stoppered bottle until all of the water has surely separated, poured into a dry tared dish and completely evaporated in the dry air-current desiccator.

This residue will contain many volatile bodies, except such as hydrated chloral, boric acid, glycerin, alcohol, lactic acid and similar bodies insoluble in petroleum ether. It may contain volatile oils, camphoraceous bodies, phenols, aromatic acids, and volatile alkaloids, etc.; whether volatile bases or volatile acids are to be found may depend largely on the reaction of the

original liquid at the time of the distillation, as noted above.

If from the appearance several different bodies are suspected to be present, the residue is treated with a little water, a drop of cochineal added, and the liquid titrated with tenth normal NaOH solution, if acid, or with tenth normal acid with cochineal as indicator if alkaline from the presence of volatile alkaloids or otherwise. Volatile oils may generally be recognized by their odor in each case.

The aqueous distillate is next similarly extracted by common ether which is allowed to evaporate carefully in the air, and may leave bodies like hydrated chloral and many organic acids in the residue.

The ethers are allowed to *completely* evaporate from the aqueous distillate and any alcohol which it contains distilled off through a distilling tube and estimated in the distillate, in case the previously found bodies are present in sufficient quantity to prevent its calculation from the specific gravity of original distillate.

Traces of glycerin, boric acid, etc., may still remain in the distilling flask. For further study the main reserved portions of the ether separates from the distillate may be shaken with a measured volume 4% (normal) NaOH solution and the latter separated. It is then titrated with normal acid, a slight excess being finally added, and shaken out with ether, which besides phenols may remove other acidic bodies, as well as aromatic acids when present. Phenols and similar compounds, however, will remain mostly in the aqueous solution. The ethers are then similarly extracted with acid water (about normal or half normal acid) which will remove any volatile alkaloids when present. Remaining in the ethers are perhaps bodies like camphors, naphthalene,

thymol, apiol, caffeine, and possibly traces of iodoform which are crystalline, and finally, volatile oils, etc., which are liquid.

SPECIAL CLASSES OF LIQUIDS

Liniments are, as a rule, of not very diverse composition, with the exceptions of some old and proprietary formulas which are well-marked exceptions to this rule. They are mostly either oleaginous mixtures or solutions of bodies, chiefly volatile, in alcohol. The ammonia liniment of the pharmacopœias is simply an ammonia soap, formed by shaking about equal measures of ammonia and olive oil together. Others, as for example, the camphor liniment or so-called camphorated oil of the Pharmacopœia, are simply solutions of camphor or other volatile bodies in oil, while an alcoholic solution of soap, with the addition of small amounts of volatile oils, form the basis for many more, to all of which may be added such substances as chloroform, menthol, volatile oils, etc.

From mixtures of the first class the oils or fatty bodies may be separated by the commonly employed methods, generally by petroleum ether or common ether, and in the case of soaps, after liberating the fatty acids by a slight excess of mineral acid, any volatile oils, camphors, etc., being first separated by steam distillation from the original mixture. From oily mixtures of the second class added bodies may frequently be extracted directly by about 75% alcohol, a procedure which also often answers in the case of melted salves. In any case the fats or fatty acids are identified from the constants given in Table VI.

From mixtures of the third class, the alcohol and other volatile liquids may be removed and separated by careful fractional distillation from a flask heated in a water-bath and any fixed residue examined as usual.

In the rarer cases where the mixture consists mostly, or even entirely, of mixtures of various volatile oils, fractional distillation will seldom accomplish the desired result and the ingenuity of the analyst will generally be taxed to its utmost for a method.

Emulsions. Emulsions intended for internal administration are frequently of such an appearance as to lead the analyst to suppose them liniments in the absence of other information, and indeed some liniments are emulsions. They are mostly mixtures, containing in the neighborhood of from 10 to 50% of fatty oils or resins, held in a fine state of subdivision and suspension in water by means of gums, pancreatin, Irish moss mucilage, yolk of egg, saponins, casein, etc., although occasionally they consist simply of a gum-resin like asafetida ground up with water.

By acidifying the mixture and allowing it to stand in a hot-water bath for some time, these mixtures will generally separate a clear supernatant oil (or resinous) layer, and a lower aqueous one, with an indefinite mixture between. In some cases the mixture may be diluted by shaking with water, and the fat separated in a Babcock centrifugal machine, as is done in the case of milk. In other cases, the mixture is spread on strips of clean fat-free blotting paper, dried in the oven and the fat extracted in a Soxhlet or similar apparatus with ether, which latter is allowed to evaporate in a tared flask, for weight. As before, the oil is identified by Table VI, and the emulsifying agents used by special methods.

SOLID MEDICINES

Powders, Pills, Tablets, etc.

These are considered together because, with few exceptions, the same kinds of medicinal substances are apt to be exhibited in either of them, and because they differ from each other only in their form and in the possession of certain more or less inert fillings, binding materials and coatings by the last two. Capsules, wafers, etc., are other common forms in which powdered or other solid medicines are often dispensed.

The filling material most commonly employed to give proper size and consistency to the pills are powdered licorice root, starchy materials, acacia, and in many cases solid plant extracts, which in this last case generally also constitute a portion at least of their active constituents. They are generally coated with sugar, gelatin or chocolate, or in the case of those intended for disintegration and solution only in the alkaline fluids of the intestine, with keratin or possibly salol.

Tablets, as a rule, contain no filling materials other than sugar of milk, cane sugar, acacia, and frequently small amounts of talc, boric acid, oils, etc., to serve as lubricants during manufacture. They may be coated with the same materials as are pills.

With the exception of the filling materials, this class of pharmaceuticals is perhaps less apt to contain any considerable amounts of those indefinite and mostly physiologically inert vegetable bodies than are most liquid preparations. Volatile bodies are, with few exceptions, seldom found in them, but a large variety of the commoner older chemical salts, as well as many of

the newer organic synthetics, are frequently exhibited in this form.

They are, however, apt to contain one or more finely comminuted crude drugs as important constituents, and it is for this reason that a microscopical analysis along pharmacognostical lines is more often required for these than other forms of medicinal perparations. The methods to be followed in these analyses are, after removing any superficial coating, to extract the crushed powder thoroughly with alcohol and proceed as directed in Chapter VI, with the liquid extract. Then extract the residue with water for the extractives and any soluble mineral salts, and lastly, to mount and examine any organized vegetable powders which may be present, according to the methods and scheme described in Chapter VIII. It will sometimes happen too that such insoluble substances as basic bismuth salts, etc., will be included in the final residue.

OINTMENTS AND SALVES

While these consist generally of solid or semi-solid mixtures of drugs or chemicals with fatty, waxy and paraffin bases, a number of similarly appearing mixtures have made their appearance in the form of clay or other poultices, or mixtures of starchy or mucilaginous pastes with glycerin soaps, casein, or some similar vehicle. From the latter class the active bodies if any, may, as a rule, be completely extracted with alcohol, leaving the clay or other base behind in a suitable form for mineral analysis or microscopical examination. Many popular toilet creams belong with these latter.

In the case of ordinary ointments or salves, separation may often be effected by dissolving the mass in

petroleum ether when this is possible, allowing all suspended mineral and vegetable matters to completely deposit, decanting the fatty solution ·as completely as possible, and washing the insoluble residue by decantation or in an extraction apparatus with small portions of petroleum ether.

The fat solution, which should not be too dilute, is then repeatedly extracted with about 75% alcohol, which will generally remove practically all of the active bodies which had remained dissolved in the fats and petroleum ether, and the united alcoholic extracts again utilized for dissolving out any active organic bodies from the insoluble residue, after which the solution is examined as usual.

In some cases, especially where the base is practically insoluble in petroleum ether, the mineral and organic medicinal matters may be separated by simply allowing the ointment to remain in a melted condition for some time, and finally filtering it through paper in a hot-water funnel. The fat soluble medicines are then extracted in a warm separator from the melted and filtered fat by shaking with alcohol of a proper strength, generally the strongest which will not also dissolve the fatty base. Many mineral and organic matters other than vegetable materials are apt to remain with the infusible material in the filter, and are to be treated as usual.

Other solvents than petroleum ether are, as a rule, not to be recommended for dissolving the fatty bases in this process, as they give up dissolved organic matters to the alcohol only with difficulty and are moreover too soluble in that liquid.

A weighed portion, about 1 or 2 g., of the filtered base, or the residue left by driving off all traces of the petro-

leum ether, is next transferred to a dry tared flask, a measured excess of normal alcoholic potash solution added, and the whole boiled under a reflux condenser until saponification of all the fatty bodies has taken place. Generally one-half hour is sufficient. The flask and contents are then allowed to cool somewhat, diluted with water, and the excess of caustic potash titrated with normal acid, using phenolphthalein as indicator, thus giving by calculation the sponification number.

Should any appreciable amount of unsaponifiable matter remain undissolved it is generally due to paraffin bases. These may be separated by again adding a small amount of KOH solution, warming until they are entirely melted and form a clear layer on the top of the formed soap solution, cooling, filtering through a wetted filter, and washing the insoluble residue with cold water or weak alcohol until the soaps are entirely removed. The paraffins (generally petrolatum) are then dissolved off the filter by ether, which is evaporated in a tared flask for weight. The fats (or waxes) are then found by difference.

The alkaline solution of the soaps is next treated with a slight excess of hydrochloric acid, warmed until the precipitated fatty acids melt and form a clear floating layer, allowed to become cold, and the acids removed by filtration through a tared and afterward wetted filter. After drying for weight, these should have their melting point and possibly also their iodine absorption determined, after which these, with the saponification number, should allow of the identity of the original fats being found from Table VI.

CHAPTER VIII

PRINCIPLES OF MICROSCOPICAL DRUG ANALYSIS

Microscopical drug analysis aims at the identification of the one or more organized drug powders contained in a mixture, by the recognition of certain cells or cellular arrangements which are known to occur constantly in the drugs in question and to be characteristic of them.

The ease or difficulty attendant on this operation will depend largely on whether or not the particular drugs have any markedly characteristic anatomical features, and also whether these structures are preserved in their normal fresh condition, or have been distorted and discolored by admixture with other bodies. It will thus be seen that the work requires more knowledge of microscopic botany than of chemistry and that its successful pursuit, presupposes a knowledge of general plant anatomy, of the minute structures of all the particular drug powders which may occur in such mixtures, and the ability to recognize them under varying conditions.

Possessed of this information, the analyst takes careful account of all these structures from the systematic examination of a series of properly mounted slides of the mixture in question, after which he may refer to a suitable analytical key for the names of the plants yielding them, just as the systematic botanist does,

chiefly from the arrangement of the different parts
of the flower.

A number of works are now available which give
adequate description of the microscopical features of
drug powders accompanied by illustrations of each, but
no descriptions or figures can ever equal an author-
itative mounted sample of the drug itself for the final
comparison, and for this reason it is advantageous for
one having frequent use for this work to provide him-
self with a cabinet in which not only samples of the
powders themselves, but preferably also, permanent
mounted microscopical preparations of them, are ar-
ranged. A collection of typical classified mounted
slides and vials containing powder, is by all odds the
best atlas.

Where the powder consists of several drugs mixed
together the difficulty is greatly increased over that
attendant upon the identification of a single one, and
in the case of drugs which are too seldom used to warrant
a description of their anatomical features being recorded,
identification is well-nigh impossible, unless the analyst
has his attention directed by some other clue, such,
for example, as a characteristic chemical constituent,
or a distinctive physiological or sensible property.
Such cases are, however, extremely rare, and the drugs
are, as a rule, of little or no utility anyway.

<div align="center">TECHNIQUE</div>

For the examination of the starch granules and
certain other cell contents a small portion of the fresh
powder or of the residue remaining, often extracting
the soluble organic matters, may be shaken up in a
small quantity of water in a vial and one or two drops of
the liquid containing the fine suspended powder trans-

ferred by means of a pipette to the center of each of a number of one- by three-inch microscope slides, covered by three-quarter inch round cover glasses, and any considerable excess of fluid sucked up by a pipette or medicine dropper. Care should be exercised to exclude air bubbles by first touching one edge of the cover glass to the slide, and then lowering the other edge over the drop by means of a needle. As the water in these mounts dries out, it is often desirable to employ a 50% solution of glycerol instead, and where the amount of powder is very small, it may be advisable to first place a good-sized drop of water or the 50% solution of glycerin in the center of the slide, and simply stir a few milligrams of the powder into it before covering with a cover glass. These uncleared mounts are frequently used for applying micro-chemical reagents, and in these cases are nearly always made in water alone.

To apply reagents to the mount, a drop is placed at one edge of the cover glass and a strip of filter or blotting paper applied to the opposite side, when capillary attraction will draw the reagent under the cover and in contact with the powder.

For a detailed study of the cellular elements, these uncleared mounts do not answer well, and for this purpose it becomes necessary to employ as a clearing agent some substance capable of dissolving out the cell contents without appreciably distorting the cell walls. For this purpose I have found nothing better than a mixture containing four parts of chloral hydrate and one part each of water, alcohol and glycerin. Although lysol, simple hydrated chloral solution, alkalies, etc., are recommended by some.

In using the mixture, a good-sized drop or two is

placed in the center of a slide, a small portion of the
powder added, the whole covered by a cover glass, and
without pressing the latter down the mixture is heated
to active ebullition over a small flame, and then quickly
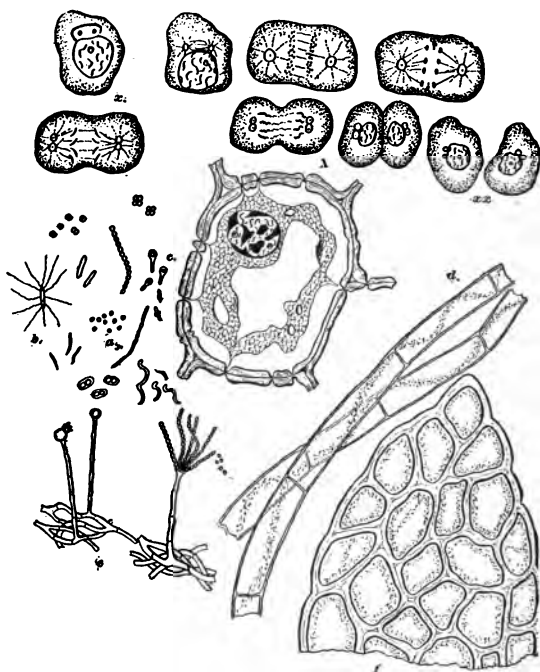
FIG. 13.

cooled by laying the slide upon a glass or other plane
surface. If the amount of clearing mixture was too
small, air bubbles will be drawn under the cover glass
on cooling, and can best be gotten rid of by allowing
an additional amount of fluid to flow under the cover
and again heating and cooling.

This treatment dissolves starch and other cell contents and renders the cell walls somewhat translucent and interesting to examine. Moreover, these mounts
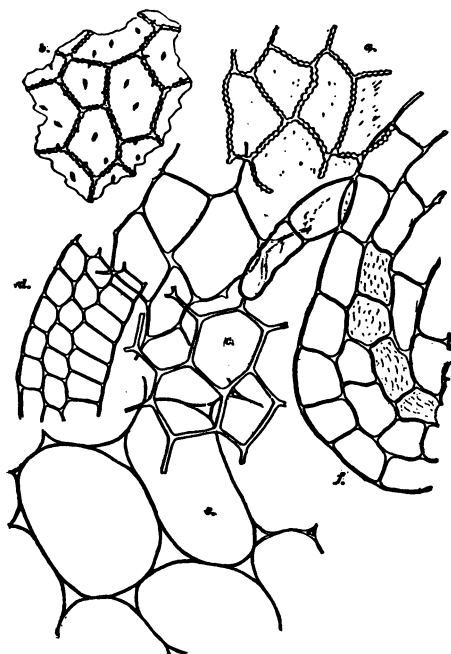
FIG. 14.

have the added advantage of being permanent for months, if not subjected to mechanical derangement.

In any of these mounts care should be taken not to crowd the slides with too much powder, as it hinders the subsequent examination, but the larger the number of slides mounted and examined the better, and, as a

rule, it may be said that this should never be less than six and preferably ten or twelve in many cases.

In the examination of the mounted slides with the microscope it is well to first gain a general impression of the field, using a magnification of from 100 to 150
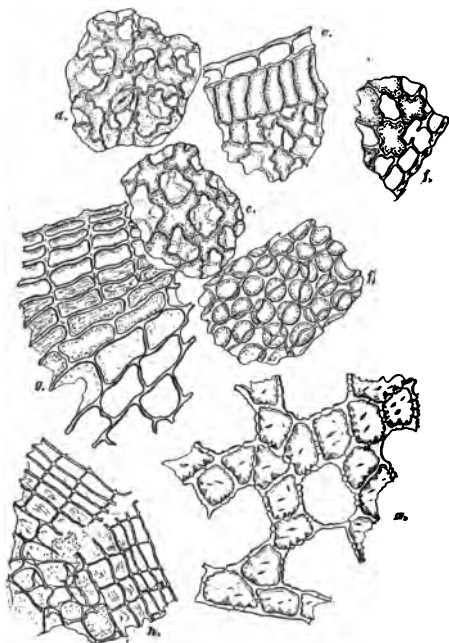
FIG. 15.

diameters, and a skilled observer will in fact seldom require a higher magnification than this, although for starch granules and other small structures a quarter-, a sixth- or an eighth-inch objective which, with an ocular, will give a magnification of from 250 to 700 diameters is sometimes desirable.

By means of the descriptions and figures following, determine the presence or absence, and the average size and shape of (1) Parenchyma cells (Fig. 14, *a–d* and Fig. 15 *a*; Fig. 13, *a–e* and Fig. 17, *d* and *e*). (2) Fibrovascular tissue fragments consisting of spindle-
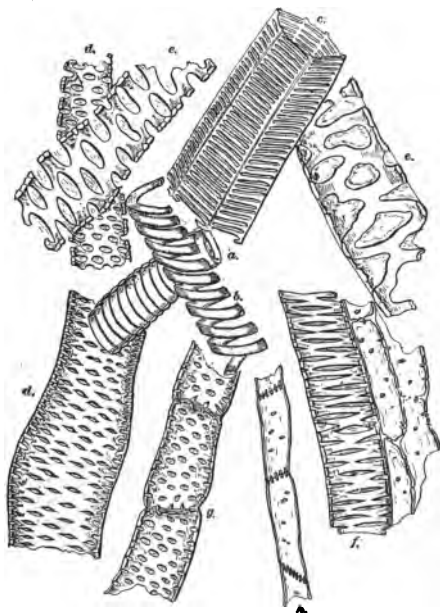
FIG. 16.

shaped wood cells (Fig. 17, *C*, No. 7, Fig. 18, *c*). Vessels and tracheids (Fig. 16, *A–G* and Fig. 17, No. 9). (3) Bast cells and fibers (Fig. 17, No. 4, and Fig. 18, *A* and *B*), and possibly delicate sieve elements (Fig. 17, No. 5, Fig. 16, *H*). (4) Short sclereids (Fig. 18, *D, F, G,* and *H*). (5) Cork (Fig. 15, *G* and *H*, Fig. 17, No. 2; Fig. 20, *J*).

(6) Portions of cortical parenchyma, etc., containing medullary ray fragments (Fig. 17, *C*, and No. 11).   (7) Patches of epidermis with stomata (Fig. 15, *D* and Fig. 19, *D*).   (8) Spongy and so-called palisade parenchyma cells, sometimes containing altered chlorophyll granules,
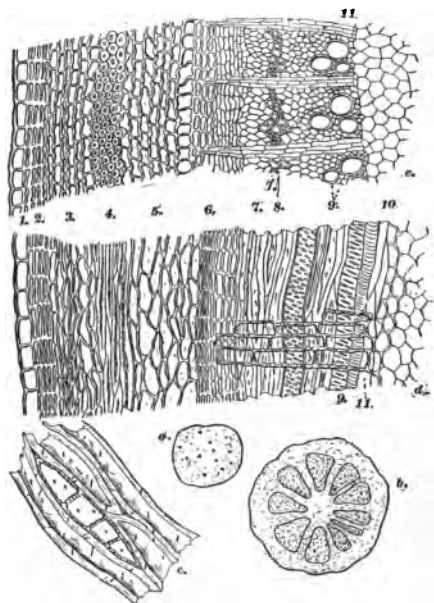
FIG. 17.

(Fig. 15, *C*, *D*, *E*, and *F*).   Such flower parts as (9) pollen grains (Fig. 22, *D*). (10) Sharply sinuate and delicate-walled petal epidermis cells, often with papillate or striate markings and nectaries (Fig. 22, *A* and *E*).   Mammillated structures from the stigma (Fig. 22, *C*) or reticulated fragments from the anther (Fig. 22, *B*).   (11) Trichomes (Fig. 20). (12) Secretion

reservoirs for latex, resins, oils, etc. (Fig. 21). (13) Starch granules (Fig. 23, *A*, *E*). (14) Crystals (Fig. 23, *F*). (15) Testa fragments from seeds (Fig. 19, *A* and *G*). Also determine the presence or absence of tannins,
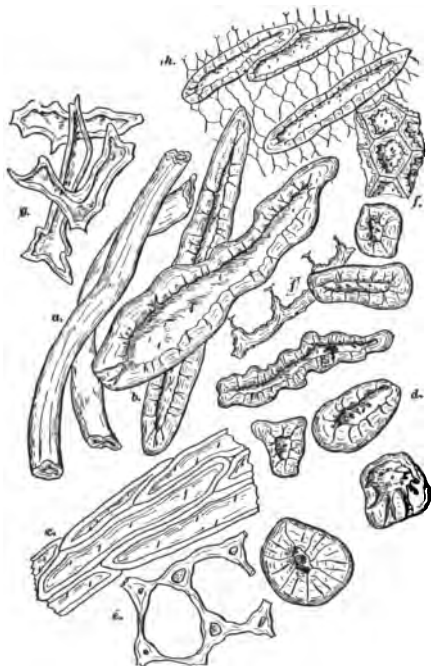
FIG. 18.

alkaloids, chlorophyll and protein granules by micro-chemical tests, if these have not already been extracted by the previous treatment of the powder, before attempting to ascertain its name from the analytical key.

The size, form, and arrangement of the different cellular elements in a drug powder are fairly constant

and characteristic, but the form and size of individual fragments of tissue are not, as these latter are due entirely to artificial conditions in the grinding, etc.,

FIG. 19.

and will necessarily vary with the fineness of the powder and the type of mill used.

As a rule, the modern disintegrators used in drug milling leave the cells in a condition more nearly approaching their natural relations one with another, than do the older processes which use more contusion. Coarse particles cannot be examined easily in powders,

so it is generally advisable to employ only such por-
tions of the mixture as will easily pass through a sieve
having about twenty meshes to the centimeter, and to

FIG. 20.

afterward reduce the coarser particles to a like degree
of fineness before examination.

Of the various micro-chemical reagents, which have
been recommended from time to time, the following six
are all that can be considered essential for the present
work.

1. A 1% solution of iodine in 2% potassium iodide

solution—colors starch a deep blue. If the wet mount be first treated with strong sulphuric acid, pure cellulose will also give a blue color with this reagent,
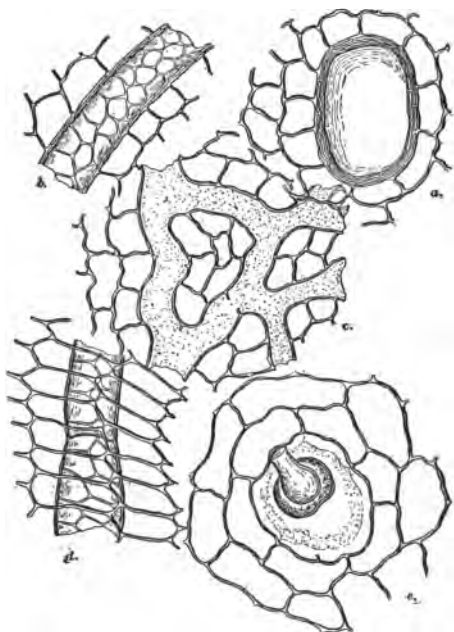
FIG. 21.

while lignified and corky tissues are colored brown or yellow.

2. A 1% solution of ferric chloride gives a greenish- or bluish-black with tannins.

3. Tincture of alkanet in 75% alcohol gives a red color with essential oils, resins, and fats. The first two being quite soluble in this strength of alcohol

diffuse about the amount, while the fixed oils and fats remain compact.

4. Solution of indol followed by 25% H_2SO_4 colors lignified tissue a deep red.

5. Millon's reagent—a fresh solution of mercury
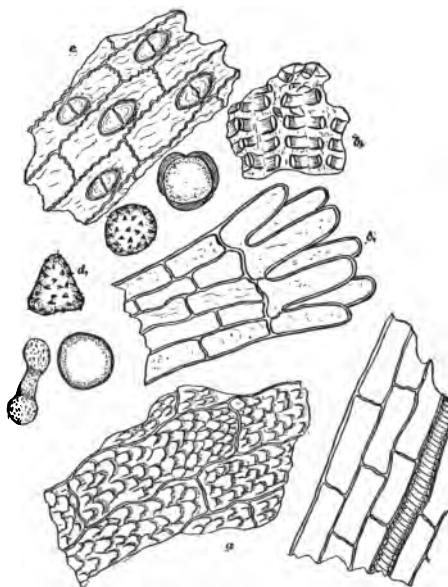
FIG. 22.

dissolved in its own weight of strong nitric acid and diluted with an equal amount of water—colors protein, when warmed, brick red.

6. Mayer's reagent gives alkaloidal precipitate when applied to a mount in 5% hydrochloric acid, but is not entirely reliable.

As the limits of size of the various cellular elements

are frequently of diagnostic importance, it is very
desirable that measurements of these be made in mi-
crons, or thousandths of a millimeter, by the use of an
accurate eyepiece micrometer or camera lucida.

FIG. 23.

In deducing conclusions from the results of these
measurements, the general average is all that can be
taken into account in most cases, and not the extreme
maximum and minimum figures which might be
obtained in a very few cases.   In the analytical scheme
following, measurements are generally stated as averaging
from such to such a size.   Finally, the beginning

student of microscopical drug analysis will be deprived
of much of the interest of his work and the capacity
for undertaking new investigations, if he fails to make
comparison between the various related structures
as they occur in different drugs, and to correlate these
variations with a modification of function wherever
such correlation is possible, and instead merely memorizes
the form and sizes of the different anatomical elements
for purposes of identification.   In other words, plant
anatomy, to be of most interest and value, should be
studied from the physiological and developmental, as
well as from the purely anatomical, standpoint.

PLANT ANATOMY

The unit of plant anatomy, as of all living organized
nature, is the cell.   See Fig. 13.   Cells of like kind are
united to form tissues, and these latter are united to
form organs.

The cells of the higher plants may be divided in a
general way into PARENCHYMA, including all those
cells which in their various modifications more closely
resemble the original type, especially as regards being
thin-walled, and PROSENCHYMA, or those which have
developed peculiar thickenings of their cell wall and
serve mostly a mechanical function.

The various groups of tissues, too, which have
special functions to perform, may be classified for
convenience as follows:

PARENCHYMATIC

A. Function nutrition.
>   1. Absorbing system (root hairs, epithelium, etc.).
>   2. Assimilating and aerating system (cells containing chlorophyll granules, and intercellular spaces opening by stomata, lenticils, etc.).
>   3. Storing system (tissues for reserve materials in seeds, fruits, tubers, bulbs, root-stalks, etc.).

B. Function protection.
>   4. Epidermal system (epidermis, cork, trichomes etc.).

C. Function reception of excrementary matters (largely).
>   5. System of receptacles for secretions and excretions (crystal cells, oil, resin, gum, mucilage, and latex canals, etc.).

D. Function perpetuation of species.
>   6. Reproductive system (andrœcium—cells of filament, anther, and pollen; and gynaecium —cells of style, stigma, and ovary [seeds]).

E. Function transportation.
>   7. Vascular system (vessels and tracheids, sieve tubes and sieve cells, wood parenchyma, etc.).

PROSENCHYMATIC

F. Function mechanical support (largely).
>   8. Skeletal system, wood cells, bast fibers and cells, stone cells, collenchyma, sclerotic parenchyma, etc.

First, let us consider those which are the most primitive and consequently often the least specialized. These are represented by the so-called cells of the fundamental system, the parenchyma cells. See Fig.

14.   These are usually oval or rounded in outline, except when distorted by pressure, and occur in the green live portions of the bark, of stems and roots, in leaves, medullary rays, the cambium zone, succulent portions of fruits, in the endosperm of seeds, etc., and, finally, in a more or less dried and empty condition in the center of the stem, where they constitute the pith, and the outer portion of the bark, where they make up the cork.

In certain drug powders these parenchyma cells are quite characteristic, as in the endosperm of Coffee, Fig. 14 *a*, and Sabadilla seeds, where their walls are alternately thickened and thin, giving them a beaded appearance.   In Areca and Colchicum seeds, 14, *b*, Chimaphila, Menispermum, the outer epidermis of Capsicum, and many other drugs, where their walls are pitted, and in the Areca and Colchicum, also considerably thickened.   Thickened walled parenchyma cells are also common in Anise, Caraway, 14, *c*, Nux vomica, the inner portions of Cascarilla, and in the medullary rays of Quassia, Guaiac and many other drugs.

In most cases, however, as in the majority of bark powders, those of nearly all the subterranean organs (roots, rhizomes, and tubers), and in the fleshy portions of fruits, seeds, etc., where they constitute the storing system, parenchyma cells have generally an irregularly rounded or oval form and thin walls.   See Fig. 14.

As the function of these cells becomes more special their form and arrangement become more varied. Between them, in the leaves and some other green parts, as well as in many roots, as, e.g., Calamus, Fig. 15, *A*, are found innumerable intercellular spaces for aeration of the tissues.   In the leaves, these spaces are

mostly toward the under side and are surrounded by the spongy parenchyma, the individual cells of which are mostly irregularly stellate in form, and so united by their projecting portions as to form a very loose open tissue through which the air may freely circulate, Fig. 15, *B* and *C*. The entrance to these air chambers is guarded by peculiar openings in the epidermis called stomata, which are slits whose breadth is regulated by two so-called guardian cells, Fig. 15, *B* and *D*, thus maintaining the proper relations between the amounts of air and moisture admitted to the air chambers.

On the upper surface of laterally disposed leaves, and upon both surfaces of vertically placed leaves, as, e.g., Senna and the older Eucalyptus leaves, exist rows of so-called palisade cells, the whole being called the palisade layer, from the arrangement of these cells (see Fig. 15, *E* and *F*). This layer consists of closely packed, vertically arranged cells which, like those of the spongy tissue beneath, are abundantly filled with granules containing chlorophyll, the characteristic green coloring matter of plants.

At three, or occasionally four, points on our plant stem these parenchyma cells are undergoing very active division, i.e., the plant is here growing. These points are at the growing tip, at the cambium or growing line between the wood and bark, and at the tip of the root immediately behind a layer of cells known as the root cap, Fig. 14, *f*; occasionally might be added, also, beneath the epidermis. The tissues of these points are known as developing tissue, or " meristem," as distinguished from the other permanent tissues. As the plantlet develops, these more primitive forms of cells are removed farther and farther from the source of supplies in the root, and it becomes necessary to set

apart certain of their number to act in a new capacity, viz., as transporters.

The body of the cell becomes elongated, its walls acquire certain peculiar markings—annular, spiral, dotted, or reticulate, the end walls separating two contiguous cells become absorbed, and there results one of a number of forms of vessels.   See Fig. 16.

These vessels are usually distinguished by reason of their peculiar markings before mentioned, as annular, Fig. 16, *A*, when composed of successive complete rings; spiral, *B*, when composed of a long, spirally wound thickening; scaleriform, *C*, when these markings cause a fancied resemblance to a ladder, as in Male Fern; dotted or pitted, *D*, when provided with fine pore or pits; and reticulate, *E*, when these openings are wider. In recticulate vessels where the clefts are narrow but long, *F*, it is but a short step to those designated as annular or spiral, i.e., having the clefts extending entirely around the tube.

The true vessels traverse uninterruptedly the entire length of an organ, but, there are others, equally numerous, which are relatively short and are separated from each other by pitted walls. These vascular elements are known as tracheids, *G*. Their walls are mostly pitted, although the pits are sometimes considerably elongated, giving them the appearance of reticulate markings.

Tracheids should make up the entire number of vascular elements in powdered Ipecac root, where the presence of true vessels would indicate an admixture with the less valuable stem tissues.

Vessels are absent from all powders of barks, and seeds. In the official woods as, e.g., Quassia, Guaiac, and Santalum Rub., they are nearly all of the pitted

variety and of large size, as many of them also are in in the roots of Licorice, Columbo, and in Hydrastis, Gelsemium, and Dulcamara, etc.

Spiral and annular vessels, mostly the former, occur in Squill and Colchicum root, and to a greater or less extent in all leaves, herbs, flowers, and fruits, and even forming a portion of the vascular system of woods and subterranean organs.

Another form of vascular element is the so-called sieve tubes, *H*, which are delicate, elongated structures provided with obliquely placed perforated plates at intervals. Similar but shorter structures are known as sieve cells.

These occur normally in all bark powders, but on account of their delicate makeup, they are usually hard to distinguish. They may also be found in Mandrake root, and in the capsule of the Poppy.

The true vessels serve principally for conveying water and mineral salts from the soil, up the stem to the chlorophyll cells in the leaves, a duty which is divided between them and the tracheids.

The sieve tubes and sieve cells serve principally for conveying non-diffusible albumenous substances through the plant, a use for which their anatomical structure admirably adapts them.

The vessels, united as they are to form vascular tissue, remain alone throughout a very small portion of their course, e.g., at the end of the vascular bundles in the leaves, etc. They are soon joined by another class of specialized cells whose duty it is to give stability to this otherwise delicate organism. These are the fibers, etc., which help to make up the skeleton or framework of the plant. Their union with the vascular tissue forms what is known as a fibro-vascular bundle

or the fibro-vascular system.   These bundles are dis-
tributed   differently   in   the   monocotyledons—those
plants having parallel-nerved leaves, and the dicoty-
ledons—those having netted, veined leaves.   In the
former, of which the common Indian corn may be
taken as example, they are irregularly distributed
through the fundamental tissue—see Fig. 17, A—and are
conspicuous upon pulling a leaf or stem forcibly apart as
tough threads.

In the latter plants, they occur first at four or six
equidistant points within the fundamental tissue,
forming an incomplete circle.   As development pro-
ceeds, this number is rapidly increased until we soon
have a complete circle of fibro-vascular bundles enclos-
ing a central pith, and traversed between each pair of
bundles by one or more rows of the parenchyma cells,
which connect the central pith with the outer or
cortical portion and which constitute the first medullary
rays, those radially arranged lines so conspicuous on
larger stems.   Fig. 17, B, C, D and E.

Let us now examine these fibro-vascular bundles
more closely.   Of what do they consist?   First, as we
have seen, they contain vessels.   These are most often
on the inner side of the bundle.   Farther out in a
radial direction, and usually separated from the vessels
by the bast or fibrous portion of the bundle, are the
sieve tubes.   Running from the vascular portion of
the bundle in a tangential direction and connecting
with the cells of the medullary rays, are delicate, pitted
walled cells, known as the wood parenchyma, Fig. 17,
F, which serve for conveying carbohydrates such as
starch, sugar, etc., through the plant and for storing
starch in the form of granules.

These circular bands of wood parenchyma are often

sufficiently connected to give the appearance of annular or year-growth rings to tropical woods which do not really possess them.

The fibrous portion of a fibro-vascular bundle consists of two principal parts. The bast fibers, already mentioned, Fig. 17, 4, together with the bast cells which are shorter and thicker 18, *B*, are situated externally with the sieve tubes and other sieve cells. Internally are the so-called libriform or true wood cells, 18, *C*, associated with the vessels and tracheids.

The bast cells are elongated with thick walls which are composed of several concentric laminæ, their central lumen being narrow. The bast fibers are similar but very much longer. As before mentioned, the only function of both of these is to give the necessary firmness and rigidity to the bundle, they having no conductive powers.

Internally the libriform or common wood cells serve a similar purpose to that of the bast cells and fibers externally. Their structure is also similar with the exception that they are usually shorter and more delicate, and usually have pitted walls.

It was formerly customary to classify the fibro-vascular bundle as consisting of an outer phloem, sieve, or bast portion consisting of the bast cells, bast fibers, sieve tubes, sieve cells, and an inner xylem, vascular or woody portion, consisting of the wood cells, wood parenchyma, and vessels.

It may be readily seen that these two portions occupy opposite sides of the cambium or growing line, Fig. 17, 6, the xylem or woody portion being inside this line and the phloem outside it, i.e., in the bark.

Owing to the sluggish cell division which goes on in the growing line, in the fall, the small formed wood

elements of autumn are immediately adjacent to the larger ones formed when vegetation is active in the spring, thus giving rise to the annular or year-growth rings.

While the arrangement of the sieve and vascular portions of a bundle just described is the normal or radial one, one may surround the other, when it is called a concentric bundle, or they may be side by side, when it is called a collateral bundle. Other mechanical elements of the plant are the short, so-called stone cells, or grit cells, 18, *D*, and the collenchyma 18, *E*, which are simply parenchyma cells thickened at the corners in order to give them greater stability.

Of the structures now described, the medullary ray fragments Fig. 17, *C*, *D*, and *E* may be found in all powders of the woods, and, are especially numerous in such barks as Wild Cherry and Cascara sagrada as well as in Gelsemium, Dulcamara, etc.

Long sclereids like the bast cells are found in many barks, e.g., Cinchona, 18, *B*, Sassafras, Cinnamon, etc., in many roots e.g., Spigelia, as well as in Clove stems, and many other drug powders.

The long fibers are especially conspicuous in such barks as Mezereum, 18, *A*, Cotton root, Elm, etc.

Short sclereids or stone cells are the most numerous of all, and are found in the powders of nearly all plant organs. They are especially common in Cinnamon, 18, *D*, Cloves, Allspice, Cubebs, Aconit, root Spigelia, Galls, and in Stramonium, Delphinium and other seeds, where they form part of the hard external testa. In Black Pepper, 18, *f* and *f'*, Capsicum, Fig. 19, *a*, where they are unilaterally thickened in a peculiar manner, in Quercus alba and, to a less extent, in such barks as Quebracho, Cascara sagrada, Viburnum, etc.

Tea leaves contain small characteristically irregular sclereids, 18, *G*, and the thin papery testa of the Coffee seed contains an almost continuous tissue of them. Fig. 18, *H*.

True wood cells of course make up the major portion of the powder of the officinal woods.   They are common, however in those of many roots, and rhizomes, and in the one stem drug, Dulcamara.   They are of course absent from the powders of seeds, barks, and other organs which do not contain fibro-vascular bundles.

Collenchyma cells too are common, but are usually not so conspicuous in powders as in sections.   They occur in Capsicum, Fig. 19, *B*, and in many other fruit and leaf drugs.

Over all these tissues, covering the entire plant surface is the protective system composed of the epidermis, and its appendages, the former being entirely replaced by cork when the parts become older.   The functions of this system are to prevent the entrance of poisonous gases or the exit of too much water, to keep away hostile animal enemies by means of sharp spines, as in the Thorn apple or by stinging hairs as in the common nettle, and lastly to protect the tissues beneath from other mechanical violence.

These militant duties are assumed by the cells of the epidermal system.   This tissue, which in young plants and annual herbs constitutes the entire covering, consists usually of a single or double row of thin-walled cells having a thickened exterior or cuticle which is impervious to moisture and effectually shuts out harmful matters, Fig. 19, *C*.   In many drugs, as, e.g., Capsicum, Castanea, Chimaphilla, Uva ursi, etc., this cuticle is considerably thickened.   The epidermis is a permanent structure on all monocotyledonous roots, e.g., calamus

(peeled in commerce), Convallaria, Colchicum, Veratrum, Sarsaparilla, etc., never being replaced by true cork in these drugs. When viewed vertically, i.e., perpendicular to the plane which the cell normally occupies, these epidermis cells have usually an oblong or elongated outline, which is fairly straight in the cells of most root epidermis, but strongly wavy and convol ted in the epidermis of most leaves, 19, *D*, and often made up of regular small convolutions in the epidermis covering some flower petals.   See Fig. 19, *C*.

   The epidermis cells are often variously thickened and roughened externally, often being thrown out in the form of papillæ, as occurs on the under surface of Coca leaves, 19, *F*, and very 'commonly on one surface of flower petals, as, e.g., certain parts of those of Chamomile, Pyrethrum, etc., Fig. 22, *A*. It is but a short step between the highest of these papillæ and the shortest of the simple hairs or trichomes, which are common in drugs like Peppermint, Cannabis, etc. See Fig. 20, *A*. These very short cornate hairs or trichomes are generally hard to find in powders, but the longer ones are highly characteristic for many drugs. They are usually designated as simple when they are unicellular, Fig. 20, *B;* jointed when composed of several regular tapering cells placed end to end, 20, *C*; compound when made up of several hairs united at the base, 20, *D*; short glandular when a glandular head is attached by a short stalk cell, 20, *E*, which in some cases is apparently although not actually wanting; and long glandular, when this head is attached to a long simple cell, or what is much more common, attached to the end of a row of cells, i.e., to a jointed trichome, 20, *F*.

   Short glandular hairs (as well as long ones) are common in such drug powders as those of Hyoscyamus,

Stramonium, Belladonna leaves, Eupatorium, Tansy, Grindelia, Peppermint, Hops (Lupulin), Cannabis, etc.

Simple trichomes are common in Senna, Pilocarpus, Kusso, Strophanthus, etc.   The fragments of the peculiar compound hairs of Nux vomica, 20, *G*, too have always the appearance of simple hairs in powders.   They are, however, made up of a number of slender filaments united in the form of a cable throughout their length, but grown together at their base and tip.   Compound hairs are common in the powder of Althæa leaves, Hamamelis, etc.   In the powders of Absinthium and insect flowers are also peculiar compound hairs made up of a short stalk from which delicate tapering limbs radiate in opposite directions, forming a T-shaped trichome.   See Fig. 20, *H*.

Jointed hairs are common in Digitalis, Hyoscyamus, Belladonna, Stramonium, Arnica, etc.

The short glandular trichomes of the mint family are highly interesting and characteristic.   See Fig. 20, *I*. They consist of a short cell which serves as the stalk and a ring of eight keystone-shaped cells which are the true glandular cells, the whole being covered by a layer of epidermis, beneath which the volatile oil is retained.

A short distance below the epidermis in such drugs as Cloves, Cubebs, Allspice, etc., Fig. 21 *A*, and farther from the surface in many roots and barks, 21, *B*, are peculiar passages or canals, which in various drugs may be filled with volatile oil, resin, latex, etc.   These passages or reservoirs are formed in two principal ways, either the contiguous cell walls are absorbed leaving a cavity occupying the former place of the cells, 21, *E*, or the secretion is poured out between them, forcing them apart, and eventually leaving them in a

flattened condition, forming the walls of the reservoir, 21, *A*, *B*, and *D*. The former, known as lysagenic passages, occur in Aurantii and Citrus (the peel of orange and lemon), and are especially large and long in the trees furnishing Copaiba balsam. The second form of reservoir, known as schizogenic passages, is common in the powders of Caraway, Anise, and Fennel, 21, *D*, in Angelica root, 21, *B*, and the roots of Arnica, Inula, and other Compositæ, etc.

The epidermis in older structures is partially or entirely replaced by cork or outer bark, as we commonly call it, Fig. 20, *J*, beneath which on the stem are the original parenchyma cells which were shut out from the rest by the formation of the circle of fibro-vascular bundles. All these together constitute the bark, viz., cork (or epidermis), bark parenchyma, bast fibers and bast cells, sieve tubes and sieve cells; occasionally, also, short stone cells are quite common.

The corky layer consists of dead and empty tabularly arranged cells, which form an impervious armor against the weather; occasionally this normally external structure may dip down into the underlying parenchyma in the form of more or less separated bands. All of the living cells external to this band of course have their source of nutrition shut off, and death of the whole number is the almost evitable result.

This is the cause of the separation of the scales of corky tissue known as *bork*, from our shagbark hickory and other trees, as well as from the common grape-vine and Clematis, where the circle of bork completely encircles the stem. This structure is also seen in sections of Cinchona.

We must be careful to distinguish between this bork, and what is commonly spoken of as bark, which

includes all these structures outside the cambium or growing line and perhaps some bork among them.

The cork is continually replaced from below, as it wears off externally by a layer of formative tissue known as the phellogen or cork cambium, and some of the parenchyma cells shut out or captured by the bork also become transposed into corky or protective tissue, but the majority simply perish. Thus we see that here as in some of our higher societies, the changed conditions resulting from the effort to forcibly transform members of a primitive into those of a more modern and advanced class, results in the advancement of some, but the extermination of the majority.

Cork cells are absent from powders of all the officinal woods, as only the central heart wood is employed. They are, however, present in those of most barks except Mezereum, Ulmus, Quillaja, Quercus alba, Ceylon cinnamon, etc. As before stated, they are absent from the powders of all monocotyledonous roots, as well as those of Male fern, Rhubarb, Althæa, etc.

They are of course absent from the powders of all leaves, herbs, seeds, flowers, fruits, etc.

The cells of the reproductive system which need our attention are those of the anther, which are sometimes recognized by peculiar reticulate markings, Fig. 22, B; those of the stigma, which are often papillate or mammillate, 22, C; and those of the pollen, 22, D, which may be round and smooth as in Saffron, etc., or spiney, as in Pyrethrum, Arnica, Chamomile and many other flower powders. They may be even somewhat triangular, as in Cloves. The epidermis covering the petals and, to a certain extent the sepals of flower drugs, is apt to be provided with elongated cells having finely wavy outline, Fig. 19, E, and Fig. 22, E. Densely papillated

epidermis cells are also common in these powders,
Fig. 22, A.

The seed after its maturity of course does not belong,
strictly speaking, to the mother plant, but an ability
to recognize its component parts when in a com-
minuted condition is nevertheless of as much importance
to the drug analyst as is that of any other plant organ.

The greater portion of most officinal seeds is made
up of the endosperm cells which are densely filled with
starch, protein granules, and fat, sometimes one and
sometimes the other predominating. The cells them-
selves are true parachyma cells and differ in size and
the thickness of the cell-wall. The walls in such
powders as those of Colchicum, Fig. 14, B, and Areca
being thick and abundantly pitted, while those of
Physostigma, Strophanthus, Cola, Mustard, etc., are thin.
The testa or outer hard shell of the seed may have
very diverse structures, in different drugs, Fig. 19, A
and G. They may be covered by hairs as in Nux vomica
and Strophanthus, or smooth as in most officinal seeds.
They may be provided with a testa composed of thick
irregularly shaped stone cells as in Stramomium seed,
the seed of Capsicum, Delphinium, Staphisagria, etc.,
or of thin-walled ones, as in Colchicum, Mustard, Nux
vomica, Strophanthus, etc.

One of the most important classes of objects from the
purely pharmacognostical standpoint is, however, the
cell contents. These are very varied, but for purposes
of identification are usually limited to starch granules,
crystals of calcium oxalate, protein granules, fat, alka-
loids, and tannins.

Starch granules (see Fig. 23, A, E) are absent from
Gentian, Flaxseed, Mustard, Senega, Triticum, and all
the drug powders coming from the natural order Com-

positæ, e.g., Taraxacum, Inula, Lappa, Arnica root, etc. In most other roots, rhizomes and tuber drugs they are common, as well as in many seeds and other reserve food tissues. The granules vary greatly in size. Among these drugs having mostly small (5 to 10 microns or
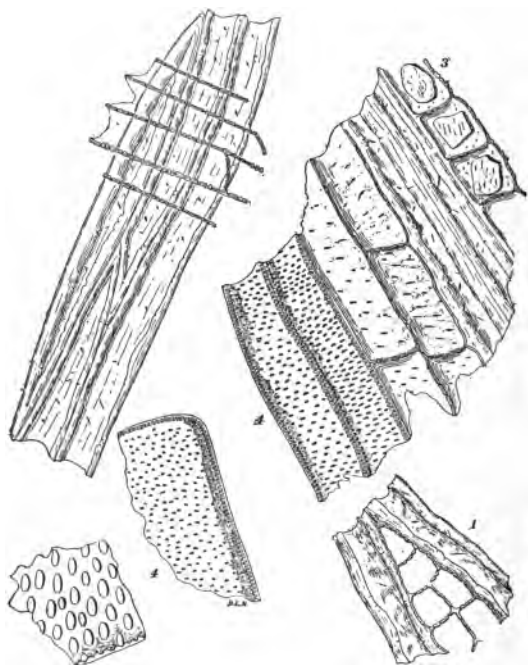
FIG. 24.

thousandths of millimeter) or very small (1 to 5 microns) starch granules may be mentioned Hydrastis, Aspidium, Glycyrrhiza, Spigelia, Caulophyllum, Cimicifuga, Calamus, etc. Among those having mostly medium-sized granules (10 to 20 microns) in their powders are Belladonna, Sanguinaria, Ipecac, Valerian, Aconite, etc.

Powders having mostly large-sized granules (20 to 40 microns) or very large ones (above 40 microns) are, e.g., Physostigma, Calumba, Stillingia, and Jalap.

Starch granules are always described as simple when alone or simply adherent in masses, and as compound
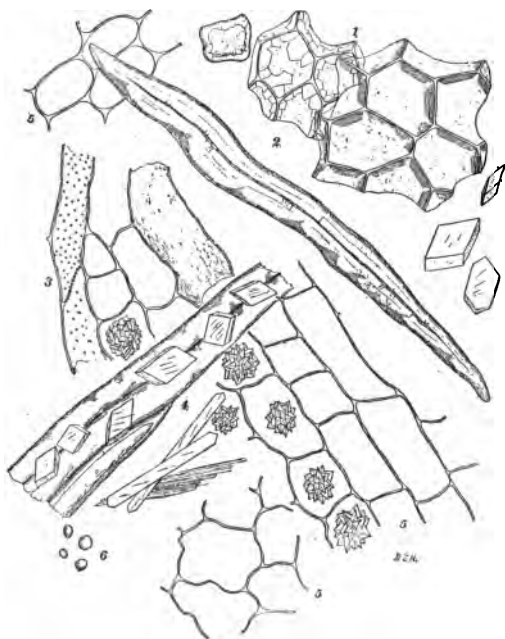
FIG. 25.

when from one to several are organically united as they are in Ipecac, Aconite root, Belladonna, Sarsaparilla, Colchicum root, Valerian, etc.

As regards shape, starch granules may be described as rounded, oval, ovate, elongated, sacciform, etc. They are organized in structure consisting of concentric laminæ deposited around the organic center

of the granule which is known as the hilum, thus giving rise to the so-called laminate markings or concentric markings. The shape and position of the hilum too is often characteristic, being sometimes placed centrally, sub-centrally, or very eccentrically, as, e.g., at the end

FIG. 26.

of one of the elongated starch granules of Ginger (see Fig. 23, *E* and *C*), and as regards shape it may be punctate, fissured, stellate, depressed, etc. Rounded granules occur in such powders as those of Rhubarb, Sanguinaria, etc., oval ones in Rumex crispus, Geranium, etc., ovate ones in Ginger, Jalap, etc., and elongated ones in Ginger,

Zedoaria, Galanga, Sumbul, etc. In certain drugs, as, e.g., Curcuma, and to a less extent in Jalap, some of the Sarsaparillas, etc., the starch granules have a more or less pasty appearance.
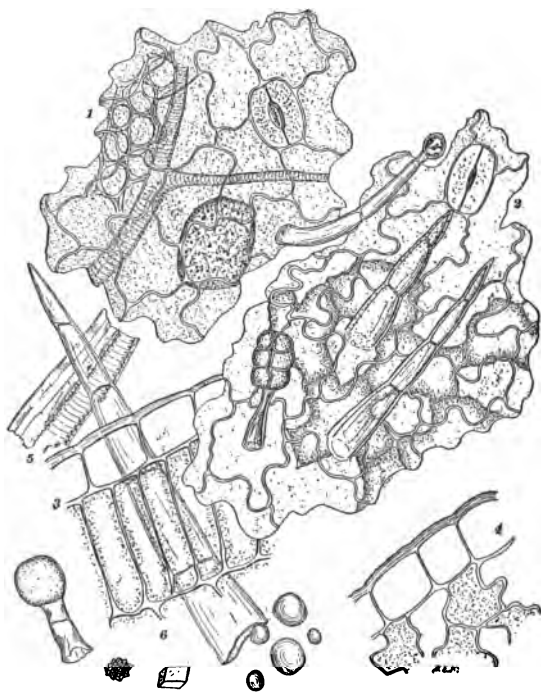
After starch granules, the next most important cell constituent which is of value to us is calcium oxalate, which exists in well-defined crystals, usually as mono-clinic prisms, coffin-shaped prisms, acicular needles, rosettes of crystals, or more rarely as in Belladonna, Tobacco, etc., in sand-like masses. Fig. 23, *F*.

Rosettes of calcium oxalate occur, e.g., in Viburnum, Mezereum, Dulcamara, Rhubarb, Rumex crispus, Podophyllum, Althæa, Krameria, Jalap, Tea, Castanea, Stramonium leaves, etc.
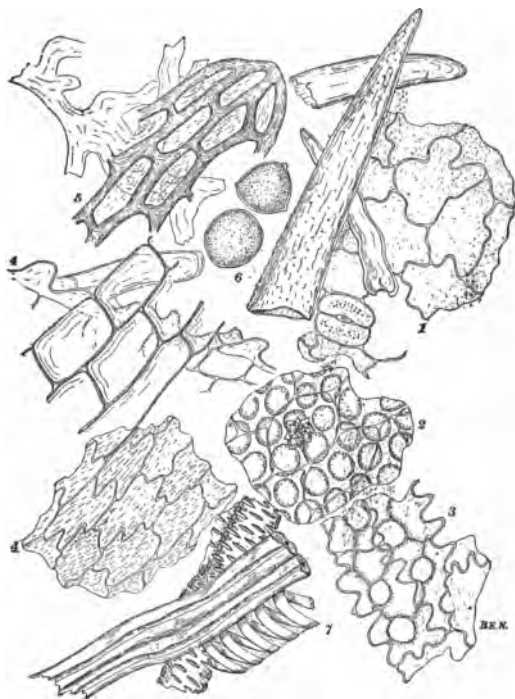
FIG. 28.

Monoclinic prisms of one or another form occur in such drug powders as those of Wild cherry, Quillaja, Ipecac, Calamus, Convallaria, Columbo, etc. In all these the crystals occur mostly free in parenchyma, while in Quebracho, Cascara, Buckthorn, Krameria, Spigelia, Glycyrrhiza, Senna, Willow bark, Coca leaves,

etc., they occur in continuous rows of nearly square
cells attached to the fibers. The rosettes too occur in
similar rows of cells in such drugs as Pomegranate
root bark.
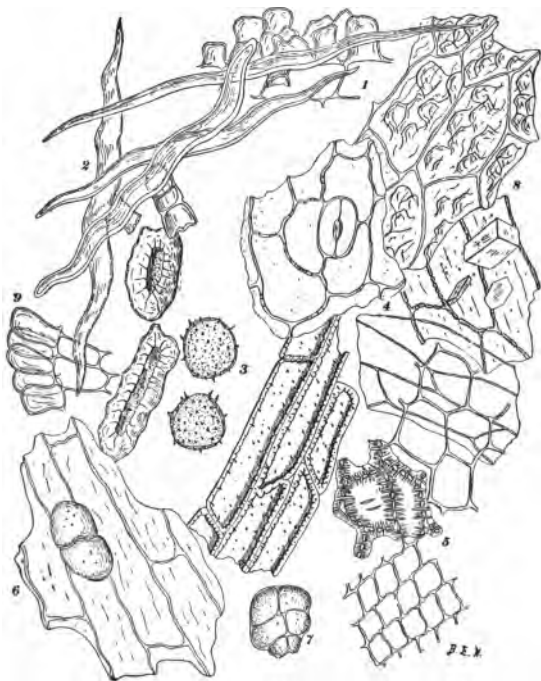
FIG. 29.

Of the drugs containing raphides, or long needle-
like crystals, Squill is perhaps the best example. Others
are Convallaria, Cypripedium, Caulophyllum, Veratrum,
Ipecac, Aconite, Sarsaparilla, etc.

From the very general anatomical survey here
presented, it may be seen that in nearly every case it

is possible to identify a comminuted drug as belonging
to one or the other of the principal plant parts of which
drugs consist, viz., woods, barks, roots, leaves, flowers,
seed, fruits, etc.

Wood powders will of course contain only wood
cells, vessels, medullary ray fragments, etc., and will
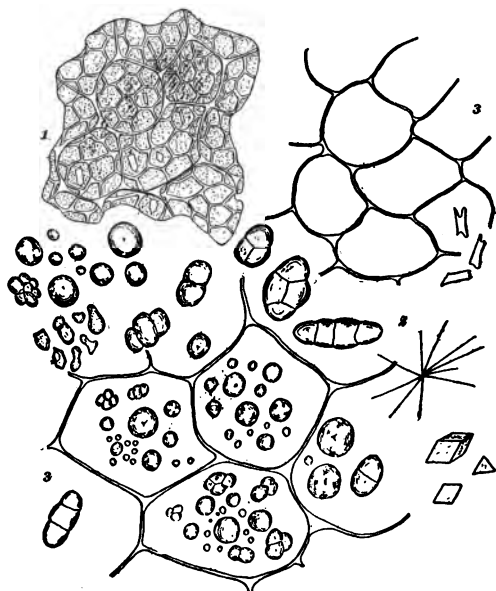
FIG. 30.

be destitute of cork, bast, etc., testa fragments and the
various special types of parenchyma cells, which belong
to other organs.   See Fig. 24.

Barks, on the other hand, will contain none of the
cellular structures peculiar to woods, with the excep-
tion of medullary ray fragments which may in some
instances extend from one into the other, but will

generally contain numerous cork masses, bast cells, cortical parenchyma cells, and frequently crystal cells, starch, tannin, etc.   See Fig. 25.

Leaves will always contain fragments made up of
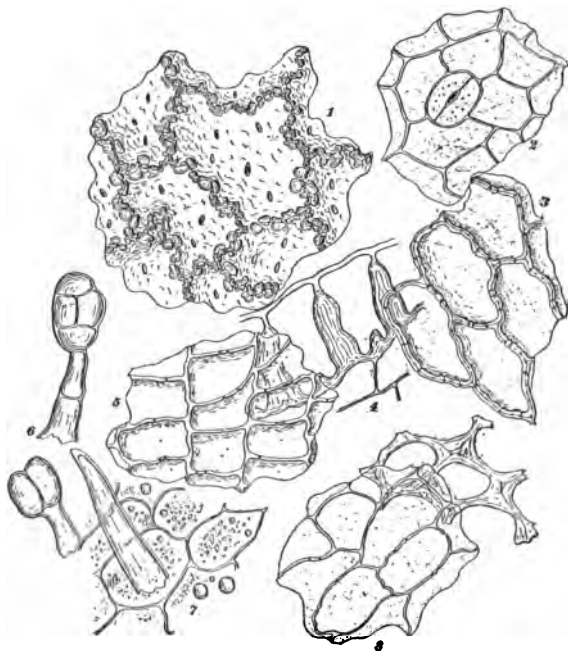
palisade cells, and of spongy parenchyma cells, in some of which traces at least of the pale yellowish-green chlorophyll masses will usually remain, and in addition will contain fragments of fine crystal cells, and trichomes.   See Fig. 27.

Seeds contain parenchymatic endosperm cells which

are always abundantly filled with starch granules, protein or fat, generally two or all of these, and nearly always a peculiarly arranged cellular structure in the testa or outer coat, which latter is sometimes provided with trichomes. Fibro-vascular tissue, cork, and leaf parenchyma, etc., are of course absent. See Fig. 30.

Roots contain varying amounts of fibro-vascular tissue, cork or epidermis cells, considerable parenchyma which in most cases is filled with starch granules, and frequently with crystals. See Fig. 26.

Rhizomes which frequently are classed with roots are in reality stem portions and contain, as a rule, a correspondingly larger amount of woody tissue. See Fig. 26.

Flowers contain a number of modified stem parts such as delicate white or yellow colored leaf-like structures which alone would never be mistaken by an experienced microscopist, but in addition, pollen grains, and characteristic structures from the stamens and pistils are present to complete the picture. Small fibro-vasuclar bundles are always found. See Fig. 29.

Fruits are of diverse structure, containing as they may chlorophyll parenchyma, sclereids, secretion reservoirs, starch, protein, vascular elements, etc., and are often best identified by a process of exclusion, i.e., by making sure that they are cellular organs which cannot be included in the other classes. This too applies to a number of special drugs which are only portions of the original plant part from which they were derived, as, e.g., Lupulin, Mace, etc. See Fig. 31.

Herbs may contain all of the above-mentioned plant organs and consequently all of the above-described celular structures. See Fig. 28.

In the following analytical scheme, the drug powders

are primarily classified in most cases according to the organs from which they were derived, this method being adopted as the most natural one, and the one capable of most useful development, as well from the scientific as from the practical standpoint.

CHAPTER IX

SYSTEMATIC MICROSCOPICAL DRUG ANALYSIS

VEGETABLE POWDERS

ANALYTICAL KEY

CLASS 1

Powders composed largely of cellular tissue.

DIVISION 1

The powder consists wholly of wood cells and vascular elements with small portions of medullary ray fragments and wood parenchyma.

Woods

A. The powder is yellowish white to light brown

Very bitter, medullary ray fragments one cell wide, wood fibers 200–500 microns x 10–15 microns, walls 3 microns, rows of crystal cells, *Surinam quassia.* (1) *Very bitter,* medullary ray fragments from two to five cells wide, vessels 25–175 microns, fine pitted 1–2 microns. *Jamaica quassia.* (1) *a.*

Not bitter, characteristic aromatic odor due to volatile oil, medullary fragments from one to four, (5–7 microns) cells in thickness, wood cells 10–15 microns, vessels 25–75 microns, rows of crystals cells. *Santalum album* (2).

B. Powder greenish brown

Very acrid taste when fresh, resinous, characteristic thick and dense-walled wood cells, 10–15 microns x 200–400 microns with walls 4-6 microns thick, often more or less twisted and gnarly, medullary ray fragments mostly but one cell wide. Wood parenchyma has thick, pitted walls, vessels 25–125 microns, with pits often in quite regular annular rows. No rows of crystal cells. *Guaiac* (3).

C. The powder is light reddish brown

1. Little or no tannin, does not color water, KOH changes color to deep red, strong HNO_3 to greenish black, medullary fragments one cell thick, wood cells 10–20 microns wide, walls 3–5 microns thick, vessels 25–200 microns. Rows of crystal cells.
Santalum rubrum (4).

2. Considerable tannin, colors water, medullary ray fragments one to two cells thick, wood cells 12–15 microns wide, walls 3–4 microns thick, crystal cells numerous. *Logwood* (5).

DIVISION 2

The powder consists of bast cells and fibers, usually stone cells, cork cells (when the cork has not been previously scraped off), portions of the medullary rays, and generally crystals of calcium oxalate.

Barks

I

CRYSTALS ABSENT OR RARE

Cork cells abundant, characteristic long sclereids 40–120 microns x 400–1200 microns, very bitter, alkaloids and tannins.

Cinchona (6).

Cork cells absent or scanty, long white sclereids, 20–30 x 250–500 microns, very few stone cells, characteristic odor due to volatile oil.

Sassafras (7).

II

CRYSTALS PRESENT

A. Prisms, mostly in rows attached to the bast fibers or long sclereids

a. Attached to large long sclereids.

Numerous stone cells 20–30 microns in groups, bitter, alkaloids, sclereids 35–85 microns.   *Quebracho* (8).

b. Attached to bast fibers.

1. Rosettes present.

No cork, numerous stone cells, much tannin, not bitter.   *Quercus alba* (9).

Cork present, few stone cells, little tannin, bright red + KOH, very bitter.   *Cascara sagrada* (10).

No stone cells, otherwise like above.

Buckthorn (11).

2. No rosettes.

Prisms abundant, few stone cells, very bitter, reactions for salicin and tannin.   *Salix* (12).

Few prisms, stone cells more numerous, tannin.

Hamamelis (13).

No stone cells. *Xanthoxylum* (14).

B. Prisms and Rosettes mostly in Parenchyma

a. Stone cells present.

1. Prisms occur along fibers, valerianic acid compounds in steam distillate, tannins, relatively few fibers. *Viburnum prunifolium* (15).

More fibers but fewer stone cells than above, otherwise similar. *Viburnum opulus* (16).

Few stone cells, rosettes sometimes in rows of crystal cells, few raphides or long prisms. *Cascarilla* (17).

2. *Prisms practically never occur along fibers.*

Prisms mostly large, rosettes in crystal rows in parenchyma cells, many medullary ray fragments, hydrocyanic acid in steam distillate. *Wild cherry* (18).

Prisms few and small, bast fibers long and silky.

Cotton root bark (18).

Rosettes frequently in crystal rows, long silky bast fibers very abundant. *Mezereum* (19).

Multitude of rosettes in crystal rows, few prisms and fibers, a few very large stone cells, alkaloids.

Granatum (20).

C. Prisms free or in parenchyma cells

a. Cork cells absent or few.

1. Containing stone cells, no raphides.

Prisms large and numerous, few stone and resin cells, 4–6 celled medullary rays, foams strongly with water. *Quillaja* (21).

Prisms very few, long white sclereids, characteristic aromatic odor due to volatile oil. See *Sassafras* (9).

Large prisms, possibly no raphides, unilaterally

thickened stone cell, characteristic aromatic odor due to volatile oil.   *Ceylon cinnamon* (22).

2. Containing stone cells and raphides.

Large prisms, unilaterally thickened stone cells, characteristic aromatic odor due to volatile oil.

Cinnamon (22).

3. *No stone cells nor raphides.*

Prisms small and few, mostly cuboid, large mucilage cells, long wavy bast fibers numerous.   *Ulmus* (23).

b. Cork cells numerous.

Stone cells and raphides. Prisms, long, raphides numerous in long bundles, many 2–3 celled medullary ray fragments and secretion reservoirs, alkaloids.

Angostura (24).

D. Prisms absent.

Rosettes often in rows, stone cells few, bitter and laxative, little or no cork.   *Juglans* (25).

DIVISION 3

The powder contains vascular elements (vessels and tracheids), wood cells and parenchyma, nearly always cork cells and starch granules (the latter replaced by inulin in the Compositæ, etc.) and frequently crystals, fibers, secretion cells, and sclereids.

SUBTERRANEAN ORGANS (ROOTS, RHIZOMES AND TUBERS)

1. Starch granules present.

A. Crystals absent or seldom found

1. Starch granules mostly small (5–10 microns) or very small (1–5 microns).

a. Stone cells absent or seldom found.

Chloral mounts colored a characteristic yellow, alkaloids, vessels mostly pitted. *Hydrastis* (26).

No alkaloids, nor yellow coloration, pitted vessels. *Cimicifuga* (27).

Numerous short pitted tracheids, possibly traces of alkaloids. *Serpentaria* (28).

Resin glands and reservoirs

Characteristic scaleriform ducts, starch granules, often irregular or elongated in form, no alkaloids. *Aspidium* (29).

Resin reservoirs, vessels mostly reticulated, no alkaloids. *Angelica* (30).

Stone cells may not be found, starch granules somewhat elongated, fibrous and woody elements numerous, possibly remains of laticiferous ducts, no alkaloids. *Apocynum* (31).

b. Stone cells are present.

Starch granules somewhat elongated, fibrous and woody elements numerous, possibly remains of laticiferous ducts. *Apocynum* (31).

Starch granules mostly very small, frequently compound, seldom elongated. *Leptandra* (32).

Small prismatic crystals may be overlooked, woody elements abundant, relatively few starch granules, alkaloids present. *Gelsemium* (33).

2. Starch granules mostly of medium (10–20 microns), large (20–40 microns), or rarely very large (over 40 microns) size.

A. Stone cells absent or seldom found

1. Alkaloids present.

Red alkaloids, starch granules nearly all simple, red resin cells, vessels mostly small, cork.

Sanguinaria (34).

White alkaloids, starch granules frequently compound, vessels frequently large, cork.

Belladonna root (35).

White alkaloids from acid solution, starch granules mostly compound or with fracture facets, hilum distinctly stellate, epidermis but no true cork, vessels small, mostly spiral, fibrous and woody elements scarce.

Colchicum root (36).

Rosettes may be overlooked, starch granules sometimes large (over 40 microns) size, many fibers, vessels reticulate or pitted, resin cells.   *Stillingia* (37).

Stone cells may not be found, starch granules mostly simple, vessels frequently large and broad pitted.

Bryonia (38).

Short prisms and stone cells may not be found, starch granules often very large (over 40 microns), small amounts of yellow alkaloid, vascular elements mostly pitted.   *Calumba* (39).

Starch granules very abundant, simple, often elongated, or sacciform, vessels mostly annular or spiral, resin cells, characteristic odor and taste, *with no cork cells* (Jamaica variety) or *with cork cells*. (African variety.)   *Ginger* (40).

Characteristic clustered starch masses and fewer simple granules, resemble those of ginger, vessels annular or spiral, chloral mounts deeply colored by the characteristic yellow coloring matter.

Curcuma (41).

B. Stone cells present

Stone cells few, starch granules mostly simple and rounded, vessels frequently large, broad-pitted or reticulate. *Bryonia* (38).

Stone cells more numerous, abundantly pitted, starch granules often compound, characteristic mammillary trichomes, odor characteristic, vessels variable, no alkaloids. *Valerian* (42).

Stone cells numerous, starch granules mostly compound or showing fracture facets, vascular elements mostly reticulate or pitted, alkaloids. *Aconite* (43).

Short prisms may not be found, starch granules often of very large (over 40 microns) size, small amount of yellow alkaloid. *Calumba* (39).

B. Crystals present

I. *Crystals mostly rosettes.*

1. Starch granules mostly small (5–10 microns) or very small (1–5 microns).

A. Stone cells absent or seldom found

Starch granules simple, frequently oval, ovate. or reniform, fibrous elements very abundant, much mucilage, no cork nor alkaloids. *Althæa* (44).

Starch granules few, simple, seldom elongated, fibrous and woody elements abundant, little alkaloid, cork. *Dulcamara* (45).

Starch granules often compound, few fibrous and woody elements, resin cells, no alkaloids. *Podophyllum* (46).

Starch granules mostly very small, large and small-sized raphides and short prisms, characteristic wavy-

walled epidermis cells, no true cork cells, vascular ele-
ments very small.   *Convallaria* (47).

B. Stone cells present

Stone cells numerous, small, starch granules mostly
very small, rounded, sometimes compound.
                                        Asclepias (48).
Stone cells less numerous but may be larger, starch
granules also somewhat larger and oval or elongated,
red with potassium hydroxide.   *Rumex crispus* (49).

2. Starch granules mostly of medium (10–20 microns)
large (20–40 microns), or very large (over 40 microns)
size.

A. Stone cells absent or seldom found

Starch granules mostly simple, rounded, no cork
cells, red with potassium hydroxide, little tannin,
rosettes numerous.   *Rhubarb* (50).
Starch granules simple, rounded, much tannin, char-
acteristic deep red coloring matter and secretion reser-
voirs, rosettes not numerous, many small prisms.
                                        Krameria (51).
Starch granules sometimes very large (over 40
microns), many fibres, few rosettes, few resin cells.
                                        Stillingia (37).
Starch granules often very large, few fibres, many
rosettes and resin cells.   *Jalap* (52).

B. Stone cells present

Starch granules may be of medium size, oval or
elongated, red with potassium hydroxide.
                                        Rumex crispus (49).

II. *Crystals mostly raphides.*

1. Starch granules mostly small (5–10 microns), or very small (1–5 microns).

A. Stone cells absent or seldom found

Starch granules mostly very small, raphides numerous and some of large size (5–75 microns), also rosettes and short prisms, characteristic wavy-walled epidermis cells, no true cork cells, vascular element mostly very small (15–20 microns). *Convallaria* (47).

Starch granules mostly very small, parenchyma cells abundantly pitted, raphides numerous but small, vascular elements small (15–20 microns), epidermis somewhat suberized but no true cork cells.

Cypripedium (53).

Starch granules mostly very small, often compounded into rounded angular masses, vascular elements of medium size (20–40 microns), cork cells.

Caulophyllum (54).

Starch granules mostly small, often compounded characteristically, alkaloids, unilaterally thickened pitted cells from nucleus sheath, no true cork cells, vessels 20–40 microns, few stone cells may be found.

Veratrum viride (55)
or *Veratrum album* (55).

2. Starch granules mostly of medium (10–20) microns, large 20–40 microns or very large (over 40 microns) size.

A. Stone cells absent or seldom found

Starch granules mostly simple and rounded, alkaloids, vascular element all small pitted tracheids, no true vessels. *Ipecac* (56).

Starch granules mostly simple, oval or ovate, with an eccentric hilum, no alkaloids, vessels quite large (20–80 microns).   *Phytolacca root* (57).

B. Stone cells present

Starch granules mostly compound or showing fracture facets, cork cells, alkaloids.   *Aconite* (43).

Starch granules frequently compound or showing fracture facets, no alkaloids, epidermis but no true cork cells, characteristic unilaterally thickened cells from nucleus sheath, rarely small prisms.
                              Sarsaparilla (58).

A few raphides may be found, starch granules mostly simple, multiform, long sclereids, vascular elements, mostly pitted tracheids.   *Spigelia* (59).

III. *Crystals mostly prisms.*

1. Starch granules mostly small (5–10 microns) or very small (1–5 microns).

A. Stone cells absent or seldom found

Starch granules not very abundant, crystals small.

Alkaloids, woody elements numerous, cork cells, vessels mostly finely pitted.   *Gelsemium* (33).

No alkaloids, fewer wood elements, vessels reticulate or pitted, prisms in rows of crystal cells attached to fibres, usually cork-cells, characteristic sweet taste.
                              Glycyrrhiza (60).

No alkaloids, wood elements few, vessels annular or broadly reticulate, prisms in crystal rows on fibres, epidermis but no true cork cells, starch granules mostly very small.   *Calamus* (61).

Starch granules very small, large raphides, no true cork cells, characteristic wavy-walled epidermis cells, vascular elements very small.   *Convallaria* (47).

B. Stone cells present

Vascular elements mostly pitted tracheids, starch granules very diverse, prisms in crystal rows on fibres, long sclereids. *Spigelia* (59).

Alkaloids, woody elements abundant, vessels mostly finely pitted. *Gelsemium* (33).

Starch granules very small, often compounded, no alkaloids. *Leptandra* (62).

A few prisms may be found, stone cells fairly numerous, starch granules mostly very small, sometimes compound. *Asclepias* (48).

2. Starch granules mostly of medium (10–20 microns), large (20–40 microns) or very large (over 40 microns) size.

A. Stone cells absent or seldom found

Starch granules relatively few, prisms short, in rows of crystal cells attached to fibres, usually cork cells, characteristic sweet taste. *Glycyrrhiza* (60).

Starch granules simple, rounded, much tannin, cork cells, characteristic red coloring matter and secretion reservoirs, very small prisms in rows of cells attached to fibres, few rosettes. *Krameria* (51).

Starch granules often ovate or club-shaped with the hilum in the larger end, many long prisms in the parenchyma, epidermis scarce, no cork, few fibres and vessels, no alkaloids. *Orris* (63).

Starch granules often very large, crystals few, short prisms, free or inside stone cells, vessels reticulate or pitted, yellow alkaloids. *Calumba* (39).

Starch granules often elongated or sacciform, vessels mostly annular or spiral, resin cells, familiar odor and taste. *Ginger* (40).

B. Stone cells present

Vascular elements mostly pitted tracheids, starch granules relatively few and very diverse, prisms in crystal rows attached to fibres, long sclereids numerous.
Spigelia (59).

Vascular elements mostly pitted vessels, starch granules numerous, often very large, crystals few, free of inside stone cell, yellow alkaloids.   *Calumba* (39).

2. Starch granules absent or accidental.

A. Inulin present in glassy masses

a. Stone cells absent or seldom found.

I. *Vessels all reticulate.*

Remains of secretion reservoirs and resin masses few or entirely absent.   *Burdock* (64).

Remains of secretion reservoirs and resinous masses numerous, feeble aromatic odor.   *Inula* (65).

Remains of secretion reservoirs, latex tubes numerous and arranged concentrically.   *Dandelion* (66).

2. Vessels pitted.

Inulin may be thought to be present, parenchyma cells regularly oblong or elongated, numerous fibres, no true cork cells (possibly few stone cells).
Triticum (67).

B. No Inulin

A. Stone cells absent or seldom found

Vessels (30–60 microns) reticulate, parenchyma cells mostly irregularly rounded or oblong, few fibres, cork cells, very bitter.   *Gentian* (68).

Vascular elements (10–25 microns) pitted, parenchyma cells mostly large, rounded, fibres numerous,

fairly thick-walled, cork cells, taste acrid, foams with water. *Senega* (69).

Vessels (10–25 microns) pitted, parenchyma cells large and regularly oblong or elongated, fibres numerous, no true cork cells, few glassy masses resembling inulin in glycerin mounts. *Triticum* (67).

B. Stone cells present

Stone cells few, vascular elements mostly pitted tracheids, parenchyma cells small, irregularly rounded or oval, fibres, cork cells, acrid taste, foams with water. *Senega* (69).

Stone cells few, vessels pitted, parenchyma cells large, regularly oblong or elongated, fibres fairly thick-walled, cork cells, few glassy masses resembling inulin in glycerin mounts. *Triticum* (67).

DIVISION 4

The powder contains patches of palisade parenchyma and of spongy parenchyma filled in the fresh condition with altered chlorophyll (some shade of green), all of which are seen through the delicate wavy-walled cells of the epidermis, which latter contains stomata. Small fibro-vascular tissues, crystals, starch granules, trichomes, oil glands, etc., more or less abundant. Pollen grains absent or accidental.

Leaves

A. Crystals absent or seldom found

a. Trichomes numerous.

Fragments of long jointed hairs and few short glandular ones, no oil glands, narcotic odor.

Digitalis (70).

Very long jointed hairs, characteristic discoid oil glands, often sandy grains, aromatic odor. *Sage* (71).

Prisms may be overlooked, long jointed and short glandular hairs.   *Rhus toxicodendron* (72).

b. Trichomes few.

Prisms may be overlooked, many finely pitted walled parenchyma cells, thick cuticle.   *Uva ursi* (73)

Rosettes may be overlooked, finely pitted cell walls, thick cuticle, characteristic masses of sphero-crystals, oil glands in axile of leaf teeth.   *Buchu* (74).

B. Crystals present

a. Trichomes numerous.

1. Crystals in fine sandy masses.

Alkaloids, fragments of long jointed and short glandular hairs.

Belladonna (75).

Jointed hairs often very large, frequently provided with glandular tips, brown color, familiar odor and taste.   *Tobacco* (76).

2. Crystals mostly prisms.

a. Unicellular trichomes.

a'. Trichomes numerous.

Characteristic slightly curved rough hairs, little spongy parenchyma, no alkaloids.   *Senna* (77).

Longer rough curved hairs, alkaloids.

Pilocarpus (78).

b'. Trichomes few or absent.

Many finely pitted rather firm walled cells, thick cuticle, few slight sclereids, no alkaloids.

Uva ursi (73).

Very few tapering thick-walled hairs, alkaloids.

Coca (79).

Characteristic large depressed stomata, angular, fairly

thick-walled epidermis cells, thick cuticle, oil cells, familiar odor.   *Eucalyptus* (80).

b. Multicellular Trichomes.

a'. Trichomes numerous.

Long jointed and short glandular hairs, few rosettes, no alkaloids.   *Rhus toxicodendron* (72).

Stellate or octopus-like hairs and few unicellular ones, no alkaloids.   *Hamamelis* (81).

Jointed hairs, with or without glandular tips, prisms often joined together into prismatic rosettes, alkaloids.
                                              Hyoscyamus (82).

b'. Trichomes few.

Hairs tapering, thick-walled, alkaloids.   *Coca* (79).

3. Crystals mostly rosettes.

A. Trichomes numerous

a'. Multicellular.

Jointed, plain and glandular hairs, few prisms alkaloids.   *Stramonium* (83).

Large jointed and short glandular hairs, few rosettes, more prisms, no alkaloids.   *Rhus toxicodendron* (72).

Compound stellate or octopus-like hairs, no alkaloids, tannin.   *Hamamelis* (81).

b'. Unicellular trichomes.

Characteristic irregular sclereids, alkaloids, tannin, familiar odor.   Trichomes tapering.   *Tea* (84).

B. Trichomes absent

(1) Crystals present, mostly prisms.

Characteristic large depressed stomata, angular, fairly thick-walled epidermis cells, thick cuticle, oil reservoirs, characteristic odor, no alkaloids.   *Eucalyptus* (80).

Few thick-walled hairs may be overlooked, alkaloids.
                                                    Coca (79).

Many finely pitted, rather firm-walled cells, thick cuticle.   *Uva ursi* (73).

(2) Crystals present, mostly rosettes.

Few pitted cell walls, masses of sphero crystals, in some large fragments remains of oil reservoirs opposite leaf notches.   *Buchu* (74).

DIVISION 5

The powder contains patches of palisade and spongy parenchyma filled in the fresh condition with altered chlorophyll (some shade of green), all of which are seen through the delicate wavy-walled cells of the epidermis, which latter contained stomata, fibro-vascular tissues, crystals, trichomes, etc., of *leaves; and in addition, such flower parts* as pollen grains, thin petal fragments with characteristic wavy-walled and papillate or striate marked epidermis cells, mammillary tissues from the stigma, etc., together with more vascular and woody elements.   *Herbs.*

A. Crystals absent or seldom found

1. Characteristic discoid oil glands, trichomes and an odor characteristic for each.

a. Trichomes numerous.

Slightly rough, long-jointed hairs, short-jointed heads and spurs, pollen rounded or slightly heart-shaped, finely echinate (18–20 microns).   *Peppermint* (85).

Jointed hairs more numerous, pollen grains 10–15 microns, otherwise similar to above. *Spearmint* (86).

A few pollen grains, etc., may be found, slender long jointed hairs, short heads and spurs, often sandy particles.   *Sage* (71).

Rosettes may be overlooked and glands mistaken,

characteristic stalked glands, resin masses, narcotic instead of aromatic. *Cannabis indica* (87).

b. Trichomes few.

Characteristic masses of spero-crystals about stomata.
Pennyroyal (88).

2. Oil glands not discoid.

a′. Trichomes numerous.

Many yellow subglobular oil glands, 30–50 microns, jointed and unicellular hairs, characteristic spiney fragments of hairy pappus, pollen rounded, echinate, 15 microns, very bitter. *Eupatorium* (89).

Fewer oil glands, characteristic " T " formed, long ribbon like or irregularly stellate hairs, pollen smooth 18–20 microns, small two-lobed oil glands, bitter.
Absinthium (90).

Small, delicate, two-lobed oil glands, imbedded in leaf epidermis, few short jointed and simple tapering hairs, pollen rounded, finely echinate, 20 microns, characteristic odor. *Tanacetum* (91).

Characteristic multicellular glands, few tapering hairs, pollen rounded, echinate (23–25 microns), acrid taste.
Grindelia (92).

3. No oil glands.

a′. Trichomes numerous.

A few pollen grains may be found, fragments of large jointed hairs, a few short glandular tipped ones, no alkaloids, narcotic odor. *Digitalis* (70).

Many long tapering, mostly thick-walled and unicellular hairs, few compound ones, pollen rounded, smooth, 15 microns, no alkaloids. *Pulsatilla* (93).

b. Trichomes absent.

Few leaf tissues, many stem elements with characteristic open spiral vessels and medullary ray fragments, alkaloids. *Scoparius* (94).

B. Crystals present

a. Trichomes numerous.

1. Crystals in fine sandy masses in parenchyma. Long jointed and short glandular hairs, alkaloids, few pollen grains may be found. *Belladonna* (75).

2. Crystals mostly prisms.

Large straight unicellular hairs, few rosettes, pollen smooth, oval, 15–20 microns. *Lobelia* (95).

A few pollen grains and other flower parts may be present, prisms often united together into imperfect rosettes, long, jointed and short glandular hairs, alkaloids. *Hyoscyamus* (82).

3. Crystals mostly rosettes.

Many characteristic stalked and sessile multicellular glandular trichomes, and short and long thick-walled, tapering unicellular ones, often with crystoliths at their base, resin, no alkaloids. *Cannabis indica* (87).

Large, straight, slightly rough unicellular hairs, few prisms, pollen smooth, oval, 15–20 microns.

Lobelia (95).

Jointed, plain and glandular hairs, alkaloids, few pollen grains and other flower parts may be found.

Stramonium (83).

DIVISION 6

The powder contains but few normal leaf structures but many modified ones, such as thin, wavy-walled and papillate or strictly marked petal fragments, mammillary tissue from the stigma, numerous pollen grains.

Flowers.

A. Crystals absent or seldom found

a. Delicate-lobed oil glands (nectaries).

1. Pollen echinate, petal fragments distinctly mammillate.

Pollen grains 18 microns, finely echinate, rounded or somewhat three-lobed, compact tissue of narrow, tapering pitted sclereids from bracts, few tapering hairs with multicellular base.   *Anthemis* (97).

Pollen grains rounded or slightly three-lobed (20–25 microns), distinctly echinate, characteristic "T" hairs, compact pitted tissues from bracts.   *Pyrethrum* (97).

Pollen grains rounded, 30 microns, distinctly echinate, oil glands on petals numerous and large, characteristic plain and glandular tipped multicellular hairs, colors chloral mounts deep yellow.   *Calendula* (98).

Pollen rounded, 30 microns, distinctly echinate, characteristic feathery fragments of hairy pappus, jointed, plain and glandular tipped hairs.   *Arnica* (99).

2. Pollen and petal fragments smooth.

Pollen three-lobed (15 microns), long wavy unicellular hairs, oil glands numerous.   *Santonica* (100).

b. Delicate oil glands (nectaries) absent or seldom found, larger oil reservoirs may be found, pollen and petal fragments smooth

Pollen somewhat triangular or rounded (15 microns), remains of oil reservoirs in parenchyma, often stone cells and elongated sclereids from stem; familiar odor.

Cloves (101).

Pollen large (90–95 microns) round, mammillate, stigmatic tissues, no other flower parts, colors chloral mounts deep orange.   *Saffron* (102).

Pollen absent, characteristic large, yellow multicellular, mushroom-shaped glands (lupulin), tapering unicellular and short glandular hairs, very wavy-walled epidermis cells, strobiles, but may be mistaken for flowers.   *Hops* (133).

B. Crystals present

I. Crystals small rosettes.

a. Delicate lobed oil glands (nectaries).

1. Pollen grains echinate, petal fragments mammillate.

Pollen finely echinate (18 microns) rounded or somewhat three-lobed, compact tissue of narrow tapering pitted sclereids from bracts, few tapering hairs with multicellular base. *Anthemis* (No. 123).

Pollen distinctly echinate, rounded or somewhat three-lobed (20–25 microns), characteristic delicate " T " formed hairs, compact, pitted, sclerotic tissue from bracts. *Pyrethrum* (No. 125).

2. Pollen and petal fragments smooth.

Pollen three-lobed (15 microns), long wavy unicellular hairs, oil glands numerous. *Santonica* (128).

b. Delicate oil glands (nectaries) absent, remains of larger oil reservoirs may be found.

1. Pollen and petal fragments smooth.

Pollen triangular or rounded triangular (15 microns), oil reservoirs in parenchyma, characteristic stone cells and elongated sclereids generally present from stem, familiar odor. *Cloves* (131).

Pollen absent, characteristic large yellow multicellular mushroom-shaped glands (lupulin), tapering unicellular and short glandular hairs, very wavy-walled epidermis cells, strobiles, but may be mistaken for flowers.

Hops (133).

2. Crystals small prisms.

Delicate lobed oil glands (nectaries), pollen echinate, petal fragments mammillate.

Pollen rounded or somewhat three-lobed (20–25 microns), characteristic "T" shaped hairs, compact pitted sclerotic tissue from bracts. *Pyrethrum* (125).

DIVISION 7

The powder consists chiefly of rounded or angular endosperm cells containing fat and protein, with characteristic patches of seed testa, and frequently starch granules and hairs. Cork cells, stomata and vessels absent. *Seeds.*

1. STARCH GRANULES PRESENT

A. *Hairs absent or seldom found*

I. Starch granules mostly small (5–10 microns), or very small (1–5).

Albaloids present

Characteristic thick, pitted-walled endosperm cells, thin-walled pigmented testa cells, color grayish brown. *Colchici semen* (134).

A few starch granules sometimes found, rounded or somewhat hexagonal, fairly thick-walled endosperm cells, and patches of dark-brown testa fragments containing radially elongated thick-walled cells, much fat, color dark brown. *Staphasagria* (152).

A few starch granules sometimes found, rounded or somewhat hexagonal fairly thick-walled endosperm cells, and more patches of dark brown testa containing nearly cuboid thick-walled cells, much fat, color dark brown. *Delphinium* (153).

A few starch granules sometimes found, hexagonal or pentagonal, thin-walled endosperm cells, light brownish-yellow testa fragments of small angular cells, color brownish gray. *Ignatia* (154).

No Alkaloids

Very small simple starch granules, much fat, acicular crystals in cooled mounts, dark reddish-brown testa fragments, fragrant odor, color yellowish brown.

Tonka (135).

Small starch granules, often compounded with a central hilum, much fat and protein, reddish brown tissue fragments (not testa), acicular crystals in cooled chloral mounts, familiar odor, color pale brown.

Myristica (136).

Great numbers of small rounded or angular starch granules, having a central hilum, testa fragments (often absent) pale yellow, containing greatly elongated fairly thick-walled cells, color white (bolted) or yellow unbolted.   *Zea* (corn) (137).

Great numbers of very small angular starch granules, often united into irregular (not oval) masses, reddish-brown testa fragments (often absent) containing elongated interlocking sclereids having a dark center, color yellowish white (bolted) or light brown (unbolted).

Fagopyrum (Buckwheat) (138).

Great numbers of very small, angular starch granules, often united into rounded or oval compound masses, testa fragments thin, color white.

Oryza (Rice) (139).

Roughened trichomes, many fragments of small oil tubes, few small bundles of raphides, very small rosettes in protein granules, characteristic odor and taste.   *Anisum* (165).

Characteristic patches of seed testa, often showing columnar patches of elongated sclereids, many tapering hair fragments, no crystals.   *Rhus glabra* (163).

2. Starch granules mostly of medium (10–20 microns),

large (20–40 microns), or very large (above 40 microns) size.

Alkaloids present

Patches of reddish brown testa having characteristic radially elongated sclereids with irregularly stellate dark cavities, color very dark brown.

Stramonii semen (140).

Brownish yellow, sometimes slightly nodular walled endosperm cells, many oval, ovate, or somewhat club-shaped starch granules, with eccentric hilum, testa fragments thin, inconspicuous, color reddish brown.

Cola (141).

Brownish yellow, distinctly nodular walled endosperm cells, few rounded or oval starch granules, yellowish white thin testa fragments with elongated, pitted or cleft sclereids, familiar odor and taste, color reddish brown.

Coffea (142).

Much fat, small stone cells, familiar odor and taste.

Theobroma (194).

Characteristic large or very large, dense starch granules, not readily cleared, testa fragments thick, with palisade layer of elongated sclereids, color brownish gray.

Physostigma (143).

No alkaloids

Great numbers of rounded or oval starch granules, testa fragments (sometimes rare) contain large, oval pitted cells often gives characteristic odor when moistened with water, color yellowish or grayish white.

Amygdalus (144).

Patches of characteristic, irregularly nodular walled testa cells, fiery color and taste.   *Capsicum* (169).

B. *Hairs present*

1. Starch granules mostly small (5–10 microns), or very small (1–5 microns).

Alkaloids present

A very few starch granules may be found, hair fragments numerous and characteristic, angular, thick-walled endosperm cells, color light brownish gray.

Nux vomica (158).

No alkaloids

Great numbers of very small starch granules which are often aggregated into rounded or oval multigranular masses, patches of elongated thick-walled cells from the testa, hairs tapering and firm-walled, color yellowish or grayish white.   *Avena* (Oats) (145).

Patches of white testa, rounded thick-walled and irregular thin-walled pitted cells, color greenish white.

Pepo (146).

Few fragments of short jointed hairs, characteristic, small, unilaterally thickened beaker cells.

Piper nigrum (159).

Few fragments of short jointed hairs, more and larger stone cells, familiar odor and taste, dark brown.

Cubeba (160).

Few unicellular hairs, oil reservoirs seen beneath epidermis, stone cells, familiar odor and taste.

Pimenta (161).

2. Starch granules mostly of medium (10–20 microns), large (20–40 microns), or very large (over 40 microns) size.

No alkaloids

Hair fragments numerous, long and slender, testa fragments contain thick-walled brownish yellow cells, few monoclinic prisms, color grayish brown.

Strophanthus (147).

Great numbers of rounded or oval starch granules (15–40 microns, averaging 20–25 microns) tapering firm-walled hairs (as large as 35x700 microns), sometimes with testa fragments containing elongated, finely pitted walled cells, color usually white.

Triticum sativum (Wheat) (148).

Great numbers of rounded or oval starch granules (5–25 microns, averaging 15 microns), tapering, usually thinner-walled hairs (as large as 150x1500 microns), sometimes with testa fragments containing elongated finely pitted walled cells, color usually white.

Hordeum (Barley) (149).

Great numbers of mostly rounded starch granules (10–50 microns, averaging 30–40 microns), tapering thinner walled hairs (as large as 20x500 microns), sometimes with testa fragments containing elongated finely pitted walled cells, color slightly grayish white.

Secale (Rye) (150).

2. STARCH GRANULES ABSENT

Hairs absent or seldom found

Alkaloids present

Rounded or somewhat hexagonal, fairly thick-walled endosperm cells, and patches of dark brown testa containing radially elongated, thick-walled cells, much fat, color very dark brown. *Staphisagria* (151).

Rounded or somewhat hexagonal, fairly thick-walled endosperm cells, and more patches of testa containing

nearly cuboid, thick-walled cells, much fat, color very dark brown.   *Delphinium* (152).

Hexagonal or pentagonal, thin walled endosperm cells, light brownish yellow testa fragments, composed of small angular cells, color brownish gray.

Ignatia (153).

Few small crystals, endocarp and endosperm cells resemble those of anise, mouse-like odor with caustic potash, no oil tubes.   *Conium* (173).

No alkaloids

Angular endosperm cells, characteristic reddish brown testa fragments, familiar odor when moistened with water, color brownish yellow, or may contain turmeric root and be light yellow.   *Sinapis nigra* (154).

Angular endosperm cells, characteristic yellowish-white testa fragments, familiar odor when moistened with water, color yellowish white or may be yellow from turmeric.   *Sinapis alba* (155).

Rounded or angular endosperm cells, characteristic reddish-brown testa fragments, with elongated pitted sclereids and rounded and hexagonal cells, often a few wavy-walled cells from the husk, color grayish yellow with shiny brown particles.   *Linum* (156).

Thin endosperm cells and characteristic testa fragments with palisade layer of elongated sclereids. Alkaloids may be overlooked.   *Fœnum grœcum* (157).

Fragments of oil tubes, familiar odor.

Carum (166).

Very small rosettes in protein granules, oil tube fragments, familiar odor.   *Fœniculum* (167).

Very small rosettes with protein granules, oil tube fragments, wavy endocarp cells, familiar odor and taste.

Coriandrum (168).

Patches of brownish seed testa, characteristic odor and taste. *Cardamomum* (170).

B. Hairs present

Alkaloids present

Numerous characteristic hair fragments, angular thick-walled endosperm cells, color brownish gray.
Nux vomica (158).
Much fat, small stone cells, familiar odor and taste.
Theobroma (194).

Alkaloids absent

Roughened trichomes, many fragments of small ·oil tubes, few small bundles of raphides, very small rosettes in protein granules, characteristic odor and taste.
Anisum (165).
Characteristic patches of seed testa, often showing columnar patches of elongated sclereids, many tapering hair fragments, no crystals. *Rhus glabra* (163).

DIVISION 8

Powders often containing seed fragments with other diverse cellular structures (fruits) and other miscellaneous cellular powders.
A few vascular fragments present.
I. Stone cells present.

A. Remains of rounded oil reservoirs, aromatic.

1. Protein granules present.
Few fragments of short jointed hairs, characteristic small unilaterally thickened beaker cells, familiar odor and taste, color grayish brown.
Piper nigrum (159).

Few fragments of short jointed hairs, more stone cells, familiar odor and taste, color dark brown.

Cubeba (160).

Few unicellular hairs, many oil reservoirs seen beneath epidermis, familiar odor and taste, color brown.

Pimenta (161).

No hair fragments, strong anise-like odor, color reddish brown.   *Illicium* (162).

2. No protein granules.

No hair fragments, flower parts may not be recognized, familiar odor and taste, brown.

Caryophyllus (131).

B. No oil reservoirs nor aromatic odor, tannin.

1. Protein granules present.

Characteristic patches of seed testa, often showing columnar palisade patches of elongated sclereids, many tapering hair fragments, no crystals, color reddish brown.   *Rhus glabra* (163).

2'. No protein granules.

A few prismatic crystals, pitted parenchyma and corky tissue, few starch granules, grayish brown.

Gallæ (164).

A few stone cells may be found, powder almost entirely composed of thin parenchyma, color yellowish white.   *Colocynthis* (175).

2. Stone cells absent.

A. Aromatic

1. Remains of elongated brownish oil canals in tissue fragments, few stomata, endosperm cells with protein granules.

Small roughened trichomes, many fragments of narrow oil tubes, few small bundles of raphides, very small

rosettes in protein granules, characteristic odor, color grayish brown. *Anisum* (165).

No trichomes nor crystals usually found, fewer fragments of oil tube, regularly arranged endocarp cells, characteristic odor, color light brown.

Carum (166).

No trichomes, very small rosettes with protein granules, fewer fragments of oil tubes, characteristically arranged groups of endocarp cells and broad pitted vascular elements, characteristic odor, grayish or greenish brown. *Fœniculum* (167).

No trichomes, very small rosettes with protein granules, few oil tube fragments, few characteristic wavy endocarp cells, characteristic odor, yellowish brown.

Coriandrum (168).

2. No oil canals, but often small rounded oil cells.

a. Protein granules present.

Oil tube fragments may be overlooked, very small rosettes with protein granules, characteristic wavy endocarp cells, characteristic odor, yellowish brown.

Coriandrum (168).

Patches of characteristic irregularly nodular-walled testa cells, few glandular trichomes, fiery color and taste. *Capsicum* (169).

Patches of brownish seed testa, characteristic odor and taste, grayish brown. *Cardamomum* (170).

b. Protein granules absent.

Irregular amylodextrin granules, elongated epidermis cells, familiar nutmeg odor, light reddish brown.

Macis (171).

Small prisms and raphides of calcium oxalate, oil globules, small black seeds, angular epidermis cells, needles of vanillin in cooled chloral mounts, familiar odor, color dark brown. *Vanilla* (172).

B. Not aromatic

2. No oil reservoirs.

a. Protein granules present.

Few small crystals, endocarp and endosperm cells resemble those of anise, alkaloid present, mouse-like odor when moistened with potassium hydroxide, color greenish brown.   *Conium* (173).

Patches of brown testa fragments, small glandular bodies, grayish or greenish brown.

Chenopodium (174).

b. Protein granules absent.

The powder consists almost entirely of delicate-walled parenchyma, color yellowish white.

Colocynthis (175).

The powder consists of parenchyma, occasional epidermis patches with stomata, and many bundles of raphides of calcium oxalate, color yellowish white.

Scilla (176).

The powder contains much wavy-walled epidermis tissue, and many mushroom, hood, or subglobular-shaped, light yellow, reticulate, glandular bodies, yellowish green.   *Humulus* (133).

Rosettes of calcium oxalate and small starch granules, many fibrous elements, color yellowish white.

Althæa (54).

No vascular fragments present.

1. Stone cells absent.

Few small prisms, large mucilage cells, and many long bast fibres, yellowish white.   *Ulmus* (26)

Radially arranged multicellular glands, color brick red.   *Kamala* (177).

The powder consists of characteristic mushroom, hood-shaped or subglobular reticulate glands, color brownish yellow.   *Lupulin* (178).

The powder consists of characteristic tetragonal, or somewhat rounded reticulate spores, bright yellow.

Lycopodium (179).

The powder consists of fragments of mycelium resembling very small parenchyma, fat drops, small violet-colored masses in chloral mounts, color purplish brown.

Er₂ota (180).

CLASS 2

Powders composed mostly of cell contents.

DIVISION 9

The powder consists of mostly amorphus cell contents often with traces of cellular remains.

A. The powder is white or yellowish white

a. Not pasty with cold water.

1. Consists entirely of granules.

Granules small (5–10 microns) or medium (10–20 microns) sized, often angular, central hilum.

Amylum (Corn) (181).

Granules mostly medium (10–20 microns) or large (20–40 microns) size, mostly oval, hilum indistinct.

Amylum (Wheat) (181).

Granules mostly large (20–40 microns) or very large (over 40 microns) sized, clam-shaped, distinct laminate markings and concentric hilum.

Amylum (Potato) (181).

Granules mostly large (20–40 microns) sized, laminate markings, hilum often eccentric. *Maranta* (182).

Granules mostly very large (over 40 microns), laminate markings and eccentric hilum, often with truncate processes.

Sago (183).

b. Pasty with water.

Yellowish white granules mostly large or very large, swollen and fissured.   *Dextrin* (184).

2. Does not consist of granules.

Few remains of greatly swollen cell walls and starch.
                                        Tragacanth (185).

No swollen cell walls nor starch granules.
                                        Acacia (186).

B. The powder is yellow

Few pitted stone cells and crystals, remains of parenchyma, etc., bright yellow.   *Cambogia* (187).

c. The powder is red or brownish red

Dark red, practically no cellular remains, much tannin.   *Kino* (188).

Light reddish-brown, cellular remains and crystals, tannin.   *Catechu* (189).

D. The powder is brown

1. Yellowish brown.

Few stone cells and elongated sclereids, few crystals aromatic, bitter.   *Myrrha* (190).

No sclereids, more crystals very bitter.
                                        Aloes (191).

2. Light brown.

Alkaloids, few cellular remains.   *Opium* (192).

No alkaloids, a few crystals and cellular remains.
                                        Aloes (191).

3. Chocolate brown.

Alkaloids, starch in granules and masses, small stone cells, other cellular remains and few crystals.
                                        Guarana (193).

Alkaloids, much fat and cellular remains, with small stone cells and endosperm cells, starch granules, sugar, familiar odor and taste. *Chocolate* (194).

No alkaloids, benzoic acid sublimes, few cellular elements. .   *Benzoinum* (195).

E. The powder is gray

Greenish gray, elongated sclereids and fibres, stone cells, few epidermal tissues and crystals.

Scammonium (196).

Brownish gray, rounded granular masses, few cellular elements. *Ammoniacum* (197).

CHAPTER X

ASSAYS OF CHEMICALS, CRUDE DRUGS, AND PHARMACEUTICAL PREPARATIONS

THE object to be attained in this work is of a different nature than that of the operations described in the preceding chapters. Here the sole aim is to measure the purity of a chemical, or the amount of the one, or sometimes two, known pharmacologically active ingredients of a drug as accurately as possible for purposes of evaluation.

While the importance of this work was originally perhaps rather slow in becoming appreciated, it has for some years probably occupied the attention of American pharmaceutical chemists more than any other one line of research, and indeed, with the exception of the improvement of a few minor details, it is doubtful whether future chemical methods will ever insure much better results than did some of the older ones. This is especially true in the case of the common alkaloidal drugs.

It is unfortunately true that the final " modus operandi" of some of our most important drugs is still not known with certainty. Absolute accuracy, here as elsewhere, is of course an ideal condition only, but with care all practical requirements may be met by most of our present processes.

CHEMICALS

The assays of inorganic chemicals and most of the common organic ones are made, generally volumetrically, by weighing and dissolving a small definite amount of the material, and titrating to the completion of the reaction with a standard normal or decinormal solution of the reagent, added a few drops at a time from a burette. For the purpose of determining the exact end of the reaction, a few drops of a solution of some suitable indicator is added to the substance, which generally, by a change of color, will indicate the first slight excess of the reagent used.

The standard solutions (see Appendix) used, are to be carefully prepared of such a strength that in the case of the normal ones, each liter will accurately contain the molecular weight of a univalent substance expressed in grams, or one one-thousanth of this in each cubic centimeter. In the case of bivalent or trivalent substances, one-half or one-third of this quantity is used. The student will readily see that from the law of definite proportions this means that each cubic centimeter of such a solution used as reagent, is equivalent to one one-thousandth of the molecular weight expressed in grams of the substance acted on if it be univalent, or to one-half or one-third of this quantity if it be bivalent or trivalent. Decinormal and other still more dilute solutions are made by diluting the normal ones the required number of times with distilled water, or by weighing the corresponding portion of the original substance for one liter. Example: the molecular weight of univalent silver nitrate is 168.69, and this number of grams of the pure dry salt dissolved up to one liter, will give a normal solution; but as this is

for most purposes inconveniently strong, a tenth or decinormal solution containing 16.869 g. per liter is used, each cubic centimeter of which is equal to, e.g., 0.005806 g. of univalent common salt, with a molecular weight of 58.06, or to 0.009926 g. of bivalent calcium bromide with a molecular weight of 198.52.

The standard solutions most commonly employed are the normal and tenth normal acids (sulphuric, hydrochloric, oxalic, and nitric), and alkalies (sodium hydroxide, potassium hydroxide, alcoholic potassium hydroxide, and sodium carbonate), tenth normal iodine, sodium thiosulphate and potassium permanganate, although the United States Pharmacopœia and works dealing with special fields of analytical chemistry recognize many more.

As it is difficult except in a very few cases to obtain chemicals of a sufficiently definite composition to admit of weighing them directly for these solutions, it is customary to prepare one or more accurately and to check the remainder against these, e.g., from a normal sulphuric acid all the alkalies may be standardized, and from these all of the other acids. Against the tenth normal oxalic acid may be checked the tenth normal potassium permanganate. Against the hydrochloric acid may be checked the tenth normal silver nitrate, against the latter the tenth normal iodine, and against this last the tenth normal sodium thiosulphate. The normal sulphuric acid itself is prepared of such a strength that 10 cc. will yield 1.1589 g. of barium sulphate. In place of this some analysts prefer to start from sodium carbonate prepared by igniting the purest sodium bicarbonate, from the purest attainable oxalic acid containing two molecules of water of crystallization, from pure native calcium carbonate, etc. These solutions do not as a rule keep well for any great length of

time, but when their strength varies they may still
be used by checking them against a solution of known
normal strength.

———————

Each cubic centimeter of *normal* acid is equivalent
to the following quantities of the various chemicals.

Ammonia gas	0.01693
Ammonium hydroxide	0.01793
Ammonium carbonate	0.047705
Ammonium carbonate U. S. P.	0.052003
Arsenous oxide.	0.025
Carbon dioxide	0.0220
Calcium hydroxide	0.03678
Calcium carbonate	0.049675
Gold (oxalic)	0.0655
Lead acetate	0.188075
Lead acetate basic	0.135935
Lithium carbonate	0.036755
Magnesium	0.0120
Magnesium carbonate	0.048226
Magnesium oxide.	0.02003
Manganese dioxide (oxalic)	0.04318
Nitric oxide (as ammonia)	0.0540
Phosphoric oxide	0.0355
Potassium acetate (ignited)	0.09744
Potassium bicarbonate	0.09941
Potassium bitartrate (ignited).	0.18678
Potassium carbonate	0.068635
Potassium citrate (ignited)	0.10736
Potassium hydroxide	0.05574
Potass. and Sodium Tart. (ignited) . .	0.14009
Potass. permanganate (oxalic)	0.031396
Sodium acetate (ignited)	0.13510

Sodium benzoate (ignited) 0.14301
Sodium bicarbonate 0.08343
Sodium borate (cryst. in glycerol), . . .   0.18966
Sodium carbonate 0.052654
Sodium hydroxide 0.03976
Sodium salicylate (ignited) 0.15889
Strontium 0.0438
Zinc oxide 0.04039

Aconitine 0.6406
Atropine. 0.2870
Berberine. 0.335
Benzaldehyd 0.1052
Brucine 0.3913
Cephaeline. 0.2314
Citral 0.7604
Cinnamic aldehyd 0.6666
Cinchonidine 0.2920
Cinchonine 0.2920
Cinchona alkaloids (total) . . . .   0.3069?
Cocaine 0.3009
Coniine 0.1262
Emetine 0.2453
Gelsemine 0.4080
Hydrastine 0.3803
Ipecac alkaloids (total) . . . .   0.2384?
Morphine crystals 0.3009
Morphine (dry) 0.2830
Physostigmine 0.2732
Pilocarpine 0.2066
Protein 0.0875
Quinine 0.3218
Strychnine 0.3317
Veratrum alkaloids 0.6870

Each cubic centimeter of *normal* alkali is equivalent to:

Acetic acid	0.05958
Ammonium chloride	0.05311
Borneol	0.15298
Bornyl acetate	0.19468
Boric acid (in glycerol)	0.06154
Citric acid (cryst.)	0.06950
Hydriodic acid	0.12690
Hydrochloric acid	0.03618
Hypophosphorous acid	0.06553
Lactic acid	0.08937
Menthol	0.15498
Menthyl acetate	0.19668
Nitric acid	0.06257
Oxalic acid	0.06255
Phosphoric acid (with phenolphthalein)	0.048645
Potassium dichromate	0.14614
Sulphuric acid	0.048675
Santalol	0.22052
Tartaric acid	0.07446
Trichloracetic acid	0.16212

Each cubic centimeter of tenth normal silver nitrate is equivalent to:

Allyl isosulphocyanate	0.016869
Ammonium bromide	0.009729
Ammonium chloride	0.005311
Ammonium iodide	0.014383
Barium chloride	0.020676
Bromine	0.007936
Calcium bromide	0.009926
Calcium chloride	0.005508
Chlorine	0.003518

Ferrous bromide 0.010711
Ferrous iodide 0.015365
Hydriodic acid 0.012690
Hydrobromic acid 0.008036
Hydrochloric acid 0.003618
Hydrocyanic acid (first precipitate) . .   0.005368
Hydrocyanic acid (with potass. chro-
    mate) 0.002684
Iodine 0.012596
Lithium chloride 0.0042
Lithium bromide 0.008634
Lithium 0.0007
Potassium bromide 0.011822
Potassium chloride 0.007404
Potassium cyanide (first precipitate) .   0.012940
Potassium iodide 0.106476
Potassium sulphocyanate 0.009653
Sodium bromide 0.010224
Sodium chloride . . . . : . .   0.005806
Sodium iodide 0.014878
Strontium bromide (cryst. with 6
    water) 0.017647
Strontium iodide (cryst. with 6 water).   0.022301
Zinc bromide 0.011181
Zinc chloride 0.006763
Zinc iodide 0.015835

Each cubic centimeter of tenth normal sodium chloride equals:

Silver nitrate 0.016869
Silver 0.0107

Each cubic centimeter of tenth normal iodine solution equals:

Antimony 0.0060
Arsenic 0.00372

Arsenic trioxide 0.004911
Antimony and potassium tartrate . . .   0.016495
Hydrogen sulphide 0.0016915
Mercury . . . .   0.0100?
Potassium sulphite (2 water) 0.009648
Sodium bisulphite 0.005168
Sodium thiosulphate, (cryst. 5 water) .   0.024646
Sodium sulphite (cryst. 7 water) 0.012520
Sulphur dioxide 0.003180
Sulphurous acid 0.0040735
Tin (as sulphide) . . . .   0.059?

Each cubic centimeter of tenth normal sodic thiosulphate equals:

Bromine 0.007936
Copper . . . .   0.00315?
Chlorine 0.003518
Chromium trioxide 0.003311
Iodine 0.01259
Potassium bromate 0.002764
Potassium chlorate 0.002028

Each cubic centimeter of tenth normal potassic permanganate equals:

Bismuth (as oxalate) 0.0104
Calcium oxide (as oxalate) 0.000278
Calcium carbonate (as oxalate) 0.0053
Formic acid 0.0046
Glycerin 0.0047
Hydrogen dioxide 0.001688
Iron (*ferrous*) 0.005550
Iron carbonate (*ferrous*) 0.011505
Iron oxide (*ferrous*) 0.007138
Iron sulphate (*ferrous*) 0.005085

Iron sulphate (cryst. 7 water) 0.027601
Iron oxide (*ferric*) . . . .   0.015864?
Oxygen 0.000794
Oxalic acid (cryst. 2 water) 0.006255
Sodium nitrite 0.0034285
Zinc (as sulphide) 0.00327

CRUDE DRUGS

Sampling. The best of assay work must fail in its object if done on improperly selected samples. To this end representative handfuls should be taken from all parts of the bale or other package, coarsely comminuted, mixed in a broad flat heap, quartered, opposite quarters rejected, and the remainder again successively mixed and quartered until the lot is reduced to 50 or 100 g. This is now finely ground or divided, again well mixed, and the quartering down continued until two lots of 10 or 15 g. each are finally reached, which lots are taken for the assays.

Extraction. Most vegetable drugs are extracted according to the directions of the pharmacopœias by the maceration of 15 g., preferably with mechanical shaking, with the subsequent removal of an aliquot portion corresponding to 10 g. of drug for assay, or what is sometimes more reliable, by the maceration of 10 g. completed by percolation to complete exhaustion, with the same solvent.

While custom has rendered these simple operations popular, it is still questionable if the samples may not be more readily and equally as surely extracted in one of the forms of continuous extractor, especially when ether or some other low-boiling solvent is used, which does not subject the delicate extracted principles to the action of too much heat. It is generally desirable

when assaying for alkaloids to first moisten and dry the drug at a very gentle heat with milk of magnesia, lime water, weak ammonia or other weak alkalies to liberate the alkaloids, before proceeding with the continuous extraction. As solvents for extraction by maceration various modifications of the original Prollius' fluid have been most used. This consists of ether, 250, chloroform, 80, alcohol, 25, and stronger ammonia 10. A marked improvement in the use of this was introduced by Keller, who macerates a weighed portion of the dry drug with ten parts of a mixture of ether and not over 25% of chloroform; after adding one part of 10% ammonia and agitating thoroughly before continuing the maceration. The later addition of the ammonia causes the drug to agglutinate, leaving a clear supernatant solvent for removal, and also by penetrating the cells displaces the organic solvent originally in them. A common procedure is to macerate 15 g. of drug with 150 cc. of solvent, add 15 cc. of ammonia, agitate, and after sufficient time to remove 100 cc. (supposed to represent 10 g. of the drug) for assay. By whatever method extracted the ethereal solution is, as a rule, finally treated in one of two ways—either A, it is transferred to a separator and the alkaloids shaken out by a succession of small portions of a 1% acid until a few drops fail to give a cloudiness with Mayer's reagent (generally 15, 10, 10 and 5 cc.), or else, B, as in the methods of Lyons and Kebler, the ethereal solution is mixed with a little weak acid and allowed to evaporate, the alkaloids going into solution in the acid as salts and the fats and resinous matters separating and adhering to the sides of the vessel. The residual acid aqueous solution is filtered into a separator, the resinous matters again dissolved in ether, more weak acid added, the ether again

allowed to evaporate, and the acid water in turn again washed through the filter. This is repeated until no further portions of alkaloids are removed by the acid as shown by Mayer's reagent, and the filter is well washed.

Final Separations. The acid aqueous solution of the alkaloids is generally next extracted with ether or ether-chloroform mixture until no more color is removed, the ether separates extracted once with acid water which is mixed with the main portion, the whole made slightly alkaline with ammonia and in the separator extracted with successive portions of ether or ether-chloroform mixture (generally 20, 20, 10, 10 cc.), until a few cubic centimeters when evaporated show no trace of alkaloids. The mixed ethereal separates are then allowed to evaporate in a tared dish, dried at a gentle heat and weighed as total crude alkaloids. Where chloroform mixtures are employed as solvent, the final residue should be dissolved in about 5 cc. of ether, and again dried to drive out all remains of retained chloroform.

The quantity of alkaloids is reported either from the percentage of total crude alkaloids weighed, or what is preferable, by titrating this residue with a suitable volumetric reagent where the case warrants. For the latter purpose the most generally used method is to dissolve the alkaloidal residue in a few cubic centimeters of neutral alcohol, add a measured excess of weak standard acid (fiftieth normal is convenient), a few drops of a suitable indicator, generally cochineal, and after standing until the alkaloids have surely all combined with the acid, titrating the excess of the latter with a corresponding alkali solution which just balances it. From the quantity of acid consumed by the alkaloids their quantity may be readily calculated from the factors given above under the normal acid.

While the above is undoubtedly the most desirable volumetric procedure, and the one to be followed with the drugs mentioned below, it unfortunately does not lend itself to the estimation of some bases, and in some cases titration of the acid solution of the alkaloids with Mayer's reagent, Thresh's reagent or Wagner's reagent (decinormal iodine solution) is sometimes still resorted to. In the cases of Mayer's and Thresh's reagents, the latter are added drop by drop from a burette to the acid alkaloidal solution, with constant stirring until no further precipitate is formed. The solution should contain approximately $2\frac{1}{2}\%$ of alkaloids. With Wagner's reagent, the total alkaloidal solution is added in portions with continuous shaking to a measured excess of the tenth normal iodine, and after the complete separation of the precipitate, the excess of uncombined iodine determined by titrating an aliquot portion of the clear supernatant fluid with tenth normal sodium thiosulphate solution.

It is still sometimes desirable also in special cases to determine the quantity of an alkaloid from the weight of gold or platinum left by burning the corresponding double salt with the alkaloid, obtained by precipitating the slightly acid alkaloidal solution with a slight excess of gold or platinum chloride. For the weights of gold or platinum corresponding to the several alkaloids, and for the equivalents of Mayer's, Thresh's and Wagner's reagents when used volumetrically, the reader is referred to older books.

––––––

While the methods of assay which are at any given time official in the pharmacopœias should always be rigidly followed in all cases of controversy, the methods *A* and *B*, outlined above, may be used for all of the

following drugs, employing the menstrua and immiscible solvents indicated.

Drug and Standard.	Menstruum for Extraction.	Immiscible Solvent.	Remarks.
Aconite 0.5%	70% alcohol	Ether	Method B
Belladonna leaves, 0.30% total	Chloroform 1, ether 4	Chloroform 1, ether 4	Method A
Belladonna root, 0.45% total	Chloroform 1, ether 4	Chloroform 1, ether 4	Method A
Coca leaves, 0.5% cocaine	Chloroform 1, ether 4	Ether	Method A
Hydrastis 2.5% hydrastine	Ether and ammonia	Ether	Method A
Hyoscyamus 0.08% total	Chloroform 1, ether 4	Chloroform 1, ether 4	Method A
Ergot 0.25%	Ether and magnesium oxide	Ether	Extract fat with petroleum ether, and make alkaline with magnesia
Ipecac 1.75% total	Ether 23, chloroform 7	Ether	Method A
Nux vomica 1.25% strychnine	Chloroform 22, Ether 68, alcohol 7, ammonia 3	Chloroform	Decompose brucine in alkaloidal r e s i d u e with 18 cc. of 2.5% each sulphuric and nitric acids during 10 min., and again extract strychnine
Physostigma 0.15% ether soluble	Ether	Ether	Method A: add sodium bicarbonate in place of ammonia
Pilocarpus 0.50% total	Chloroform 98% ammonia 2%	Chloroform	Method A
Colchicum seed 0.45% total	Ether 70, chloroform 20, alcohol 8, ammonia 2	Chloroform	Method B, but take up alkaloid w i t h water alone before shaking out
Colchicum root 0.35% total	Ditto	Ditto	Ditto
Coniium 0.50% total	Ether 95, alcohol 4, ammonia 1	Ether	Weigh as chloride and multiply by 0.78 for free coniine
Gurana 3.50% total	Chloroform 95% ammonia 5%	Chloroform	Method B
Cinchona 5.0% total	Chloroform 1, ether 4	Chloroform 1, ether 4	Method A

SPECIAL ASSAY METHODS

Opium. Standard about 7% of crystallized morphine for the gum opium and 12 to 12.25% for the powdered or granulated drug. Agitate 10 g. of fine opium with successive portions of water (100 cc. and 50 cc.) for several hours, washing the residue on a filter each time up to 150 cc. of filtrate. Evaporate first the weak and finally the strong extract carefully in a tared dish to 14 g., and transfer the residue as completely as possible to a 100 cc. Erlenmeyer flask, cleaning the dish with an extra 6 g. of water. To the 20 g. of fluid in the flask add 12.2 cc. of alcohol and 25 cc. of ether, agitate, add 3.5 cc. of 10% ammonia, stopper and again agitate for ten minutes, after which allow to stand for at least sixteen hours.

Decant the ether solution through a pair of counterpoised filters, extract the liquid twice more with ether, and finally add the dark aqueous liquid and suspended crystals, removing all of the latter and washing them onto the filter with water saturated with crude morphine from a previous assay. Wash them then with alcohol which has also been saturated with morphine and finally with 10 cc. of ether. Dry at 60° C., and weigh. The crystallized morphine weighed should be corrected for the matter insoluble in lime water, applied as long as it removes any alkaloid reacting with Mayer's reagent.

Digitalis (*Keller's Method*). Exhaust 20 g. by percolation with 70% alcohol, evaporate carefully, dissolve residue in water, precipitate with a slight excess of basic lead acetate, remove excess of lead from filtrate, concentrate, make alkaline with ammonia, extract completely with chloroform and allow the latter to evaporate. Dissolve the residue in 3 g. of chloroform,

add 7 g. of ether and pour into 50 g. of petroleum ether, stir continuously for some time, collect on a tared filter, and weigh as *digitoxin;* the most important glucoside in the *leaves*.

Strophanthus. Exhaust 20 g. of drug with 70% alcohol, evaporate carefully, take up residue and wash from fatty matters, precipitate with basic lead acetate, remove lead from filtrate with sodium sulphate, concentrate, extract with amylic alcohol (or chloroform) and evaporate for weight.

Anthraquinone Drugs (*Vanderkleed's Method*). Exhaust 10 g. of drug by heating with four successive portions of 2% alcoholic potassium hydroxide under a reflux condenser, evaporate to dryness, transfer residue with water to a separator (or perforator), acidify strongly and extract completely with ether. Evaporate ether to 25 cc., add an equal volume of strong ammonia, and continue the evaporation until most of the ammonia is dissipated. Add an equal volume of 10% sulphuric acid, warm on water bath for fifteen minutes, cool and filter into a separator (or perforator) and repeat warming with 10% acid until the filtrate is colorless. Lastly, again completely extract with ether and dry at about 80° C. for weight.

Standards are—Cascara sagrada 2 to 3%, buckthorn 1 to 1.25%, rhubarb 1.25%, senna 0.75%.

Aloes (*Shaefer's Method* for aloin). Dissolve 20 g. of aloes in 125 cc. of hot water, acidify with hydrochloric acid, allow to stand until resinous matters separate, filter, add 20 cc. of strong ammonia water and 15 cc. of 50% calcium chloride solution and stir vigorously. After one-half hour filter off the crystalline precipitate, decompose with a slight excess of hydrochloric acid, add boiling water just sufficient

for solution, filter and expose the filtrate to a low temperature for the crystallization of the aloin. The aloin crystals should preferably be washed with a saturated solution of aloein prepared from the same variety of aloes, and dried for weight.

Wormseed, for Santonin. Extract 10 g. for twelve hours with ether, evaporate, boil the residue with 5 g. of calcium hydroxide and 300 cc. of water, filter hot, wash, acidify and warm until santonin crystals begin to form, then add 100 g. of aluminum acetate solution, boil, evaporate to dryness on a water-bath, mix the residue with 3 g. of magnesium oxide, moisten with water, dry again, powder, extract for five hours with ether, evaporate, dry and weigh.

Tea, Coffee, etc., for Caffeine (*Keller's Method*). Macerate 6 g. of the drug with 120 cc. of chloroform, add 6 cc. of ammonia water, shake vigorously, and macerate until the solution is clear (12 hours), filter off 100 cc. of the menstruum into a tared flask, drive off the chloroform, add 5 cc. of absolute alcohol, again dry (crude caffeine), add 7 cc. of water, 3 cc. of alcohol, heat on water-bath, filter, wash with hot water, dry, and multiply weight by 20.

Cacao Seeds, Chocolate, Cocoa, etc., for theobromine. Heat 10 g. twenty minutes with 150 cc. of 5% sulphuric acid, filter hot, add excess of sodium phosphomolybdate, allow to stand one day, filter and wash with 5% sulphuric acid. Decompose the precipitate with barium hydroxide, pass carbon dioxide, filter, evaporate, and extract with chloroform. Evaporate dry and weigh for *total alkaloids*. Dissolve the alkaloids in water containing ammonium hydroxide, add tenth normal silver nitrate solution in measured excess, boil, filter, and determine the remaining silver in an aliquot

part of filtrate.   Silver multiplied by 1.66 equals theo-
bromine.

Tobacco, for nicotine (*Kissling's Method*).   Triturate
20 g. of powdered leaves with 10 cc. of 5% sodium
hydroxide in 50% alcohol, extract with ether.   Allow
the ether to evaporate in a distilling flask, make faintly
alkaline with sodium hydroxide, and distill with steam
until distallate ceases to react for alkaloids (400 cc.?).
Add rosolic acid (or cochineal) and titrate with tenth
normal sulphuric acid, each cc. of which equals
0.0162 g.

ASSAYS OF GALENICAL PREPARATIONS

A detailed account of the methods for these would
lead us beyond the limits of the present volume, but
in general the analyst who is familiar with the methods
used for the drugs themselves can easily devise mod-
ifications suitable for handling the residues from the
various tinctures, extracts, etc., prepared from them.

CHAPTER XI

PHARMACOLOGICAL METHODS

PHARMACOLOGY in its broadest sense refers literally
to drug knowledge generally, but in its more restricted
sense as now commonly applied, it refers essentially
to *the action* of drugs and chemical substances on the
animal organism. It comprehends not only the observed
effects which these substances produce on the various
vital processes and organs, commonly called pharmaco-
dynamics and physiological action, but aims to deter-
mine *how* and *why* these several effects are produced.
Another branch of the subject studies the relations
between chemical constitution (i.e., the relations of the
various atomic groups in the molecule) and physio-
·logical action. This latter subject, while yet in its
comparative infancy, promises eventually to be of
great value in predicting the probable medicinal uses of
substances, and of directing the synthesis of new
chemicals which are to have certain desired physiolog-
ical properties.

As may be readily seen, the pursuit of this subject
in its entirety presupposes a broad knowledge of phys-
iological processes, and the ability to control, alter and
demonstrate them in various ways experimentally.
The last-named branch of the subject also requires
a considerable knowledge of organic, physiological, and
physical chemistry.

All these are obviously outside the realm of the drug analyst, but an ability to determine in a *general* way the action of the *unknown* substances which he will from time to time separate, as well as of unknown mixtures themselves, is often fully as important a problem as is the chemical analysis itself.   This will be apparent when it is considered that we are as yet unable to predict with any certainty the action of any *unknown* substance, however well we may have determined its chemical and physical constants.   Only after recognizing it as a *known* drug or chemical, whose action has been previously determined by pharmacological or preferably clinical methods, is it possible for the chemist to venture an opinion regarding the probable action of a medicine.   Even pharmacological methods often fail to demonstrate in the relative short periods of time over which they are continued, actions which clinical experience has clearly demonstrated.   Examples of this exist in the cases of the use of iron in anæmia, the so-called vegetable alteratives, the bitter stomachics, etc., for while many of these are undoubtedly of some remedial value as proved by long clinical experience, experiments have not, as yet, been devised which prove the cause of this value pharmacologically.

For the present work it is assumed that the analyst will refer to standard works and current literature on therapeutics and pharmacy for the action of the more commonly used substances which he finds from his analysis of a medicine, and for the names of the drugs which yield certain proximate principles, which are frequently simply mentioned in the tables.

The actions of a few of the common drugs are shown briefly in Table IX.   Pharmacology is also as yet a comparatively new science, and to discredit results

which careful clinical observations have demonstrated as being true, simply because they cannot as yet be explained or demonstrated experimentally in the laboratory, is not as a rule justifiable.

Where both sets of observations agree, however, we can feel much more certain of our premises. Where, as is often the case, the analyst can obtain data from reliable sources bearing on the action of an unknown medicine which he has to examine, it is generally better to accept these than the results of the comparatively few animal experiments which he will be able to make.

This is especially true of drugs or combinations of drugs whose effects are slowly produced, as distinguished from the more potent poisons whose action is as a rule much quicker.

It must not be forgotten too that the lower animals often differ markedly from man in their susceptibility to the action of many chemicals, and it is well known that human beings also differ in this respect.

While some drugs act largely on account of their physical properties, e.g., saline laxatives, oils, etc., most act by their chemical effects on certain cells or cell constituents, as a rule either stimulating or depressing the physiological action of these cells.

The observed effects of a medicine are, consequently, often the resultant of its stimulating effect on some groups of cells and depressing effect on others. It is also true that a very large dose of a stimulating substance may be followed by immediate depression or even paralysis.

Pathological conditions which cause the unnatural stimulation or depression of certain cells or groups of cells, also often modify the observed effects of a drug.

Certain large groups of substances often have a very general common action, e.g., nearly all simple bitters increase the appetite and body weight, and consequently act as stomachic tonics.   This action seems apparently to be due in most cases to the bitter *taste* itself, as the injection of these drugs directly into the stomach is frequently not followed by the usual effect, which on the other hand may be produced by simply chewing the material.   Many derivatives of the methane series (aliphatic compounds) and even the hydrocarbons themselves, are depressants to the central nervous system, and as a result we here find our most commonly used anæsthetics, hypnotics and sedatives.

On the other hand many derivatives of the benzene series (aromatic compounds) are antipyretics, analgesics, and antiseptics, and most of them are poisonous in large doses.

The heavy metals too, when in solution, are more toxic than those of the alkalies and alkaline earths, the iron group occupying a somewhat intermediate position.

The methods of experimental pharmacology are essentially those of experimental physiology, and the apparatus required is the same.   For demonstration purposes, or for obtaining graphic records, the work also requires the ability to perform numerous surgical operations on animals, the directions for which may be found in works on experimental physiology.

In the way of apparatus for these latter purposes there will be needed : *First.*   A kymograph of the Ludwig pattern, which consists of a vertical mechanically revolving drum, the speed of which is adjustable to from one to three millimeters per second, and which carries a heavily glazed paper uniformly sooted over, preferably by camphor smoke, on which tracings may be

easily made by bristle, goosequill, or stiff paper points, attached to light straw levers. Many operators prefer to use fine light drawn-out glass tube pens containing ink, for obtaining graphic records. The apparatus often carries a mercury U-tube manometer and the recording levers, etc. *Second.* Several retort stands with suitable clamps for holding light balanced levers, the arm carrying the writing style being eight or ten times the length of the shorter or power end, and also supports for beakers, flasks, animal boards, etc. *Third.* One or more Marey's tambours, which are small drums for transforming pulsating movements into oscillations of the writing levers. These pulsating movements may, however, often be as conveniently recorded, as in a laid-bare frog heart, by simply connecting the organ to the short end of the writing lever by means of a light pointed straw lever, or silk thread inserted through the tip of the ventricle. *Fourth.* A mercury mano-meter for measuring blood pressure. This consists of a glass U-tube, in one arm of which floats a vertical rod, carrying a cork at its lower end, and attached to a writing lever at its upper. The other arm is con-nected by means of lead tubing with a small glass T-tube. One of the two remaining arms of this T-tube is connected by lead tubing with a funnel or small aspirator bottle containing normal salt solution (0.7%) or solution of magnesium sulphate, which may be raised or lowered to regulate the pressure, and the other arm by further lead tubing with a small drawn-out glass tube canula or T-tube, which is inserted in the artery   Short sections of rubber tubing carrying screw clamps are placed, one between the pressure bottle and one between the artery canula or T and their respective lead tubes. *Fifth.* Suitable means

of supplying normal aerated salt solutions and those
containing medicines, continuously, at blood-heat (36–
38° C.), for experiments on mammals.

Small Liebig's condensers, around which water flows at
the required temperature, and through which the physi-
ological solutions are delivered, answer well for regulat-
ing the temperature, small (150 cc.) tubulated aspirator
bottles answer well for delivering the solutions and
accurately regulating the pressure required. Air or
oxygen should be allowed to bubble through these
bottles where the solution is to largely replace the normal
blood. This serves to prevent asphyxiation. *Sixth*.
A galvanic cell and small induction coil for electric
stimulation, one or two small scalpels, dissecting
forceps, artery clamps (forceps), scissors, and an assort-
ment of different-sized glass canulæ, straws for levers,
and writing points, complete the outfit.

The animals most commonly employed for laboratory
experiments are the dog, cat, rabbit, guinea-pig, frog,
and turtle. In some cases accommodating human
friends may lend themselves to experimentation.
For most investigations of medicines there is wanted
their effects on the circulation and respiration, the
nervous system, the muscular system, the pupil, secre-
tions, and general metabolism. The last are obviously
not to be shown by graphic methods.

Demonstrations of the former are, for humanitarian
reasons, to be made on anesthetized animals, or those
in which conscious sensibility has been removed by
destroying the brain. A mixture of chloroform and
ether will generally serve best for dogs and cats, and
ether alone for rabbits and guinea-pigs. When the
action of morphine will not be objectionable, it is well
to administer about two or three milligrams per

kilogram of animal weight about one-quarter hour before beginning the anæsthesia. Chloretone, chloral, etc., may also be sometimes used in suitable doses. The operation should not begin until anæsthesia is *just* complete, i.e., until there are no voluntary movements, complete muscular relaxation, no reflexes from pin pricks, etc., and little or no corneal reflex (on touching the open eye). Respiration should be even and deep and the anæsthetic administered *regularly* so as to *just* maintain these conditions. In experiments on frogs the brain is first destroyed (pithing) or, where the operation is one causing no pain, the muscles may be paralyzed by painting a small amount of solution of curare on the animal some time before the operation. Frogs should always be kept moist.

CIRCULATION AND RESPIRATION

A. Anesthetize the animal completely and expose the carotid artery by making an incision over the trachea extending down nearly to the breast bone, carefully pushing away the fascia and muscles until the artery and pneumogastric nerve are seen. Carefully separate the fascia holding these, and close the artery with an artery clamp well down toward the thorax, and also at the upper end of the incision. Cut the artery between the clamps, insert a T-tube glass canula into the free ends and secure it firmly by ligatures, fill the free end of the T with normal salts solution (0.7%) or magnesium sulphate solution, and insert it into the short, clamped section of rubber tubing attached to the lead tube of the U manometer, which has also previously been filled with a warm salt solution. Likewise fill the tubulated bottle or funnel with warm salt

solution, and raise or lower it until it indicates a pressure of about 130 mm. on the mercury of the manometer. Connect the vertical float in the opposite limb of the mercury U-tube with a writing lever. Open the trachea just below the larynx and introduce one branch of a large stout T-tube toward the lungs, and secure it firmly by twine. Continue giving the anesthetic now through this T-tube. Connect one of the remaining open ends of the incubation T-tube in the trachea with a Marey's tambour, and this again with a second writing lever, which should be arranged to oscillate against the revolving drum in a vertical line, either above or below that from the mercury manometer.

Avoid surgical injury to other organs than those operated on, *especially* the pneumogastric nerve. With care little or no loss of blood need occur except while cutting through the skin and superficial fascia. For injecting the medicine, or more generally the weaker solution of it in salt solution, the jugular vein (near the carotid artery) may be clamped by a pair of artery clamps (forceps), the vein cut between them and a glass canula inserted into the end nearest the heart for infusing the drug solution. The latter is best delivered in normal salt solution at a temperature of 36 or 38° C., from a pressure bottle connected by means of a rubber tube with the glass canula, and elevated so that the inflow when the lower artery clamp is removed will be gradual. The clamp is kept on the vein except when making injections. When operating on rabbits the jugular vein need not be opened, but instead, the medicine may be infused through a large hypodermic needle, inserted toward the head into one of the large veins on the margin of the ear. The needle may be connected by a rubber tube to the pressure

bottle as before, or to a large aspirating syringe, which with its contents, is to be kept warm before use by immersion in water at 38° C.

When everything is in adjustment, start the drum at a rate of from one to three millimeters per second, remove the clamps from the carotid artery, see that the recording levers work properly, note the time, and take a normal record extending over several minutes. Now inject a suitable portion of the medicine, make two slight marks on the record paper to indicate the duration of the time of the injection, and continue the experiment, if possible until normal conditions again begin to be restored. If the effects of the drug are transitory, it is sometimes possible to keep the animal alive sufficiently long for a second injection and record. Finally, again noting the time, push the anesthetic (here preferably chloroform) until death results.

It is very convenient to have a small electromagnetic marker connected with the revolving drum and with a clock, which mechanically records the second marks on the paper along with the other tracings.

In this and all similar experiments, it is highly essential that all conditions of temperature and especially pressure be maintained constant before and after the injection of the medicine, as otherwise an increase or diminution of blood pressure may escape notice or be misinterpreted. Most medicines require to be previously prepared for injection, by concentration, freeing them from alcohol, solution and clearing, or even the separation of active bodies, before mixing with the salt solution. The tracings consist of wavy lines shown in Fig. 32, *A*, the upper showing the blood pressure, and the lower the respiration, on the dog.

B. Destroy the brain of a frog, expose the heart,

and connect the ventricle with a writing lever by means
of a light straw or light silk thread passed through the
point of the organ by means of a fine needle.   Keep-
ing the frog moist with a wet cloth, take a normal
record while the heart is continuously bathed in a nor-
mal salt solution (not very warm).   Now mark the
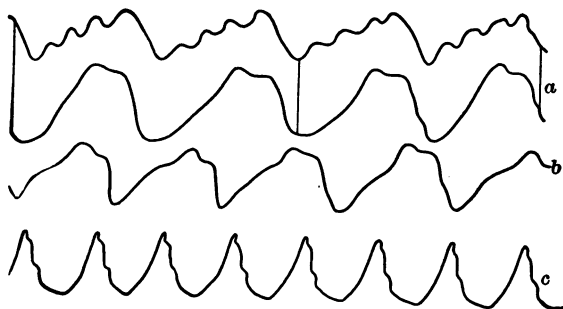record and change the irrigating solution from normal

FIG. 32.—a Tracings of blood pressure (upper) and respiration (lower)
curves, on dog. b Direct tracing from frog's heart. c Sphygmo-
graphic pulse tracing. Speed, 10 mm. per second.

salt solution to normal salt solution containing quite
a strong solution of the medicine, and continue the
experiment as before.   Or a much weaker solution
of the medicine in normal salt solution may be infused
through the heart by a small glass tube canula inserted
into the inferior vena cava, cutting one branch of the
aorta for the escape of the excess blood and fluid.
Lastly, kill the animal.   The record tracing consists
of waves such as are shown in Fig. 32, B.

NERVOUS SYSTEM

BRAIN

The more immediate effects of some medicines, as, e.g., caffeine, on the brain, are shown by changes in the phenomena of cerebration. These are best studied by psychological methods which often are with difficulty applied to the lower animals, and the ingenuity of the experimenter will often determine the success of the experiment. With an intelligent dog by artfully placing small portions of desired food where the exercise of considerable intelligence will be necessary for securing them, and comparing the periods of time required for this with similar periods after the administration of the medicine, some success may sometimes be had. Here caution must be exercised to avoid confusion owing to the uses of other senses as, e.g., that of smell, in place of those intended. Again it may be possible to compare the reaction times between the seeing of a stick thrown, after several misleading false movements, and the commencement of the journey after it.

In general, however, in these cases, it is more conclusive, when possible, to conduct the experiment on the human subject, and to compare the accurately measured reaction times of answering a series of questions requiring some thought, with those similarly obtained after taking the drug.*

In the case of medicines producing more profound results, as in the cases of hypnotics, narcotics, and sedatives generally, it is usually sufficient to carefully

* Small time intervals may be measured by the tracings produced on the smoked paper of the drum, by a short bristle attached to the tine of a vibrating tuning fork of definite pitch.

observe the effects on dogs, the rapidity of action, degree of narcosis, duration, etc., as well as the after effects.

NERVES AND MUSCULAR SYSTEM

REFLEXES

Destroy the brain and medulla of a frog, attach a short quill or stiff paper writing lever at right angles to the leg, and suspend the animal against a board in such a manner that movements of the foot will be recorded on the smoked drum. Start the latter revolving and, with watch in hand, touch the foot with the wires from the battery through which a weak induced current may flow from the induction coil. Note exactly the time in seconds when the foot draws up, and see that it is recorded on the paper strip. Repeat the stimulation *at regular intervals* of time for an average. Now inject the medicine into the dorsal lymph sac, mark the record, and after a quarter or half hour continue the experiment as before. This gives a measure not only of the reaction time to stimulation, but also of the relative strength of the reflexes.

MUSCULAR SYSTEM

Carefully separate the calf muscle (gastrocnemius) of the leg of the frog with a scalpel, cut the heel tendon (tendo Achillis) at its attachment, and fasten it by a silk thread to a writing lever. Also expose the sciatic nerve at its origin in the lumbar plexus.

Having adjusted the frog and writing lever so that contractions of the muscle will be recorded on the drum, start the latter revolving and, *at regular time intervals*, slightly touch the sciatic nerve with the tip of a feather,

or when this fails to produce a satisfactory reaction, with the wires carrying a weak electric current. Mark the record and attach a 30 g. weight also to the heel tendon, and repeat the stimulations at regular intervals as before until the muscle is distinctly fatigued. A suitable quantity of the medicine is now injected into the dorsal lymph sac, the muscle tendon and nerve of the other leg exposed and adjusted as before, and, after a quarter or half hour, the experiment repeated exactly as in the first instance.

These tests are designed to show not only the effects of the drug on the contractions of the muscle, but also the amount of work which the latter is capable of performing before fatigue. Alcohol, e.g., hastens, cocaine or caffeine delays, fatigue.

THE PUPIL

The effect of many chemical substances on the pupil of the eye, whether applied directly or administered internally, is so characteristic and so easily demonstrated, as to make it of prime importance to the drug investigator. The cat, dog, and rabbit generally answer well as experimental subjects. The solution to be dropped into the conjunctiva should be nearly neutral in reaction and fairly concentrated. In this place it is only possible to mention a few familiar substances as, e.g., atropine, hyoscyamine, cocaine, etc., which dilate the pupil, and opium, physostigmine, pilocarpine, etc., which contract it.

SECRETIONS

In determining the effects on the various glandular secretions (saliva, perspiration, urine, etc.), it is generally sufficient to compare the quantity of these with the

normal quantity, both being determined over a period sufficiently long to avoid error. It is well in the case of the urine to make some observations of the amount and also of the solid matters excreted, of the presence or absence of the administered drug in the urine, and in the case of medicines intended for use in diseases of the genito-urinary tract, of a tendency toward any antiseptic action which would retard bacterial growth. Experimental animals must, for these tests, be kept in cages which will allow of securing the excretions.

GENERAL METABOLISM

The effects of medicines on metabolism are as a rule often so slowly produced that for anything approaching reliable information, observation must from necessity be continued over a considerable period of time, a like period of time being also required for establishing a "normal." It is also well to employ a series of animals, the "normals" of some corresponding with the "time during administration" of others. Records should be kept of the daily gain or loss in weight, and of any other observed changes.

SIMPLER METHODS

While the preceding is a hasty review of the laboratory methods commonly employed in studying, and especially in recording for demonstration purposes, the action of drugs, it may be remarked that a skilled diagnostician will generally be able to observe all, or nearly all, of the above facts, and frequently many more. Moreover this may often be accomplished without recourse to laboratory apparatus or surgical experiments on animals. This is especially true of observa-

tions on the human subject, which has, of course, been most studied.

Slight changes in the respiration are apparent to the senses of the trained observer, and the same is true of the variations in the strength of the heart beats (pulse), and even to variations in the arterial tension (pressure). The reaction time and extent of muscular reflexes may be determined on the human subject, and the effects on the nervous system, secretions, pupil, and general metabolism, are best determined by direct observations in any case.

When, however, it becomes desirable to express graphically or numerically certain of these effects, it is of course necessary to employ suitable apparatus. Changes in the circulation may be observed in the pulse and shown on tracings by the sphygmograph, of which the Dudgeon type is a commonly used one. This instrument is simply strapped on the wrist. A button, whose pressure may be adjusted mechanically, is arranged to bear over the artery as the finger would do in the ordinary operation of feeling the pulse, and the motion communicated to it by the pulsating artery is communicated to a series of magnifying levers which trace the magnified motion on smoked paper in the form of waves. See Fig. 32, C.

Considerable practice is required with each instrument to secure accurate adjustment and pressure on the artery, so as to avoid artificial results.

For measuring variations in the blood pressure, there are now on the market a number of sphygmomanometers whose principle of action is essentially the same. Each consists of a firm inflated ring which connects by means of a firm tube with a mercury column or spring gauge dial. The ring is secured around an

extremity, and air pumped into it until the superficial circulation is stopped by pressure. This pressure is now very gradually relieved until the first return of the circulation, when the pressure on the gauge or mercury column is read off.

The strength of muscular contractions and their resistance to fatigue may be measured by a number of forms of dynamometers, of which Mosso's ergograph is an example.

The list might be extended to include all the commonly used clinical and diagnostic apparatus, but enough has been said to emphasize the fact that however valuable laboratory pharmacological experiments may be for purposes of instruction, they cannot, as yet, supersede the facts which the skilled physician or other trained observer is able to secure by clinical methods, and the analyst is again urged to secure such data whenever they are available from reliable sources.

TABLES

TABLE I

SYSTEMATIC TABLE OF ORGANIC DRUG CONSTITUENTS AND MEDICINAL CHEMICALS

I. VOLATILE WITH STEAM

A. EXTRACTED BY ETHER

A. *Extracted from ether by 4% caustic soda solution from which it may be again liberated by acids and again extracted and recovered by ether.*

Boiling-Point 175–186. Melting-Point −58. C, 58.82%; H, 9.81%; O, 31.37%..........VALERIC ACID.

Odor characteristic, as is also the ester formed by heating with amylic alcohol and sulphuric acid. Precipitated by aluminum sulphate and silver nitrate, but not by lead acetate. Soluble in water, alcohol, ether, chloroform, benzene and petroleum ether.

B.P. 200–220° C. M.P. below −25° C. Average elementary analysis: Carbon, 67.7%; Hydrogen, 6.5%; and Oxygen, 25.8%.

BEECHWOOD CREOSOTE.

Aqueous solutions give a reddish brown precipitate with bromine water and a blue violet color with ferric chloride. Odor characteristic. Specific gravity 1.078–1.080. Soluble in ether, alcohol, chloroform, benzene, and slightly in petroleum ether, but practically insoluble in water.

259

M.P. 28.5° C., B.P. 200–205.   C, 67.74%; H, 6.45%;
O, 25.81%..........................Guaiacol.

Specific gravity 1.170.   Soluble in alcohol and ether nearly insoluble in water, insoluble in benzene and petroleum ether.   Blue changing to greenish with ferric chloride.

M.P. 40. B.P., 175–185.   C, 76.59%; H, 6.38%; O,
17.03% ....Phenol.

Soluble in water, alcohol, ether, benzene and slightly in petroleum ether.   Aqueous solutions give a white precipitate with bromine water and a blue violet color with ferric chloride. Odor characteristic.

M.P. 45.   C, 60.00%; H, 8.00%; O, 32.00%.

Angelic Acid.

Soluble in alcohol and ether.   Precipitated by lead acetate.

M.P. 50–51.   C, 80.00%; H, 9.33%; O, 10.67%.

Thymol.

Characteristic odor.   Specific gravity 1.030.   Soluble in alcohol, ether, chloroform, benzene, etc.   Insoluble in water. No color reactions with strong sulphuric acid or ferric chloride. Liquefies when triturated with camphor or menthol.   A few drops of sulphuric and nitric acids added to an acetic acid solution produce a bluish green color.   Chloroform added to a warmed sodium hydroxide solution give a violet color.

M.P. 82.   C, 71.42%; H, 9.52%; O, 19.06%.

Diosphenol (Barosma camphor).

Soluble in alcohol and ether, and sodium hydroxide solution, from which latter it is precipitated by carbon dioxide. Deep blackish blue color with ferric chloride.

M.P. 85–87.   C, 65.69%; H, 5.11%; O, 29.20%.

Guaiacol Carbonate.

White crystals soluble in alcohol, ether, chloroform and benzene.   Easily saponified by solutions of sodium or potassium hydroxide and on then acidifying gives a distillate of guaiacol

(which see) with steam. No color reactions with strong sulphuric acid or ferric chloride.

M.P. 114. I, 100%. ....IODINE.

Volatile in the air, decolorized by caustic soda solution, the neutral solution giving a yellowish white precipitate with silver nitrate which is insoluble in nitric acid and ammonia. Solutions color starch blue. Soluble in aclohol, ether, chloroform, benzene and in solutions of potassium iodide.

M.P. 121. C, 68.85%; H, 4.91%; O, 26.24%.
BENZOIC ACID.

Neutral salts give a flesh colored precipitate with ferric chloride. No color reaction with strong sulphuric acid. Sublimes readily in fine needle-shaped crystals. Soluble in alcohol, ether, chloroform, benzene and slightly in petroleum ether.

M.P. 122. C, 83.33%; H, 5.55%; O, 11.12%.
BETANAPHTHOL.

Yellowish white crystals soluble in alcohol, ether, chloroform and alkalies. No color reaction with sulphuric acid, greenish changing to brown with ferric chloride, a blue fluorescence with ammonium hydroxide, and a blue tint changing to green and finally to brown on heating a sodium hydroxide solution containing some chloroform. Bromine water gives a white precipitate soluble in ammonium hydroxide.

M.P. 133. C, 72.99%; H, 5.41%; O, 21.60%.
CINNAMIC ACID.

White crystals soluble in alcohol, ether, chloroform and benzene.

M.P. 152. C, 62.50%; H, 4.16%; O, 33.34%.
ANEMONIN.

Colorless crystals with an acrid taste, easily soluble in alcohol and chloroform, difficultly soluble in ether.

M.P. 157. C, 60.87%; H, 4.34%; O, 34.79%.
SALICYLIC ACID.

White crystals, soluble in alcohol, ether, chloroform,

benzene.   No color   with   sulphuric   acid, a   deep blue   violet
with   ferric   chloride,   and   an   odor   of   wintergreen   on   heating
with   methyl   alcohol   and   sulphuric   acid.

M.P. 187.   C, 60.00%;   H, 8.00%;   O, 32.00%.
CAMPHORIC ACID.

White   needles.   Rotates   plane   of   polarized   light   48
degrees right.   Soluble in alcohol, ether and chloroform but
only very slightly in water.

M.P. 218.   C, 64.51%;   H, 6.45%;   O, 29.04%.
CANTHARIDIN.

Pale   yellowish white   crystals.   Soluble   in   all   common
organic solvents.   Neutralized by alkalies it gives precipitates
with   lead   acetate,   barium   chloride,   mercuric   chloride,   etc.
0.0001 g. will cause blisters on the skin.

B. *Not extracted from ether by soda solution but extracted by hydrochloric
acid solution*

B.P. 3.5° C.   C, 61.02%;   H, 15.25%;   N, 23.73%;
O, absent. . . . . TRIMETHYLAMINE.

Ammoniacal odor, alkaline reaction.   Hydrochloric acid
salt   melts at   271–275,   and   the   picrate at   216.   Soluble   in
alcohol, water and ether.

B.P. 7.2.   C, 65.64%;   H, 15.15%;   N, 18.21%;   O,
00.00%. . . . . DIMETHYLAMINE.

Hydrochloric acid salt melts at 176 and picrate at 155.

B.P. 18.   C, 53.22%;   H, 15.64%;   N, 31.14%;   O,
00.00%. . . . . ETHYLAMINE.

B.P. 117.   C, 39.91%, H; 13.40%;   N, 46.69%;   O,
00.00% . . . . ETHYLENE DIAMINE.

Clear thick white liquid.   Specific gravity 0.970.   Alkaline
ammoniacal odor, soluble in water, alcohol and in ether but
nearly insoluble in benzene.

B.P. 166. C, 76.81%; H, 12.00%; N, 11.20%; O, 00.00%............................Coniine.

Alkaloid. Precipitated by platinic chloride from acid solutions, M.P. 175, by gold chloride, M.P. 77, by picric acid, M.P. 75. Right rotary 15.5 degrees. Soluble in alcohol ether, chloroform, benzene and slightly in petroleum ether.

B.P. 210. C, 68.78%; H, 12.10%; N, 8.91%; O, 10.21%...........Valyl (Valeryl diethylamide).

Colorless liquid. Soluble in water, alcohol and ether.

B.P. 247. C, 74.08%; H, 8.64%; N, 17.28%, O, 00.00%............................Nicotine.

Left rotary 161 degrees, but the *salts* of the alkaloid are right rotary. Precipitate by platinic chloride, M.P. 275, by picric acid, M.P. 218.

B.P. 311. C, 76.92%; H, 11.11%; N, 11.97%; O, 00.00%......................Sparteine.

Soluble in alcohol and chloroform, insoluble in benzene and petroleum ether.

c. *Not extracted from ether by sodium hydroxide or hydrochloric acid, i. e., remaining in ether solution.*

1. Liquids.—Volatile liquids to be separated by fractional distillation on water-bath, and the residual oils, etc., examined by further fractioning over flame.

Boiling-Point 16. C, 32.00%; H, 6.66%, N, 18.66%; O, 42.68%....................Ethyl Nitrite.

Floated on ferrous sulphate solution in sulphuric acid gives a deep olive brown zone. In contact with sulphuric acid and potassic iodide liberates nitrogen dioxide gas, each cubic centimeter of which at 25° C. and 760 mm. pressure is equal to 0.0030736 g. of ethyl nitrite.

B.P. 19. C, 37.22%; H, 7.81%; Cl, 54.97%.

Ethyl Chloride.

Specific gravity 0.918 at 25° C.

B.P. 35.5.   C, 64.79%; H, 13.60%; O, 21.61%.

ETHYL ETHER.

Specific gravity 0.716 at 25° C.

B.P. 46–47.   C, 27.27%; S, 72.73%.

CARBON DISULPHIDE.

Specific gravity 1.256 at 25° C.   Burns readily yielding sulphur dioxide gas.   Insoluble in water, soluble in common organic solvents.   Unaffected by lead acetate, but after boiling with KOH solution gives a black precipitate of lead sulphide.   Strong solutions heated first with ammonium hydroxide and then with alcohol, give on the addition of hydrochloric acid and ferric chloride a deep red precipitate of ferric sulfocyanide.

B.P. 45–100.   C, 83–84%; H, 17–16%.

PETROLEUM ETHER.

Insoluble in water, soluble in common organic solvents except weak alcohol.   Very inert chemically.

B.P. 60–61.   C, 10.06%; H, 0.84%; Cl, 89.10%.

CHLOROFORM.

Specific gravity 1.502 at 25° C.   Slightly soluble in water, soluble in organic solvents.

B.P. 71.   C, 15.39%; H, 3.23%; I, 81.38%.

ETHYL IODIDE.

B.P. 72.   C, 54.50%; H, 9.15%; O, 36.35%.

ETHYL ACETATE (Acetic ether).

Specific gravity 0.883 at 25° C.   Saponified by boiling with potash solution yields alcohol (iodoform reaction in distillate) and acetic acid (red color of salts with ferric chloride).

B.P. 80,   M.P. 5.5.   C, 92.30%; H, 7.70%.

BENZENE (Benzol).

Specific gravity 0.884 at 25° C.   Insoluble in water, difficultly soluble in common alcohol, soluble in other organic solvents.

B.P. 96–99. C, 51.20%; H, 9.46%; N, 11.96%; O, 27.38%. ....AMYL NITRITE.

Specific gravity 0.865 at 25° C. Decomposed by potassium iodide and sulphuric acid yielding nitrogen dioxide gas. Floated on a sulphuric acid solution of ferrous sulphate the solutions give a brownish green zone.

B.P. 99–103. C, 54.52%, H, 9.15%; O, 36.33%.

AMYLENE HYDRATE.

Slightly soluble in water, soluble in organic solvents. Odor of camphor and peppermint.

B.P. 104–106. C, 61.01%; H, 11.87%; O, 27.12%.

ACETAL.

B.P. 110. C, 91.24%; H, 8.76%...........TOLUENE.

Difficultly soluble in water, soluble in organic solvents.

B.P. 123–125. C, 54.52%; H, 9.15%; O, 36.33%.

PARALDEHYDE.

Boiling with water and sulphuric acid yields aldehyde, B.P. 21° C. Heated with ammonio-silver nitrate gives a silver mirror. Slightly soluble in water, soluble in organic solvents.

B.P. 131.5. C, 12.76%; H, 2.14%; Br, 85.10%.

ETHYLENE BROMIDE.

B.P. 131.5. C, 68.18%; H, 13.63%; O, 18.19%.

AMYL ALCOHOL.

Chief constituent of fusel oil but seldom found in a pure condition, for which reason the above boiling point and elementary composition is seldom observed.

B.P. 138. C, 90.50%; H, 9.50%. ......PARA XYLENE.
B.P. 139. C, 90.50%; H, 9.50%......META XYLENE.
B.P. 142. C, 90.50%; H, 9.50%.....ORTHO XYLENE.
B.P. 148. C, 4.74%; H, 0.40%; Br, 94.86%.

BROMOFORM.

Specific gravity 2.808 at 25° C. Slightly soluble in water, soluble in organic solvents.

B.P. 155–156.   C, 88.23%; H, 11.77%......TEREBENE.
     Specific gravity 0.866 at 25° C.   Very difficultly soluble
in water, soluble in organic solvents.   Optically inactive.

B.P. 155 to ?.   TURPENTINE and other VOLATILE OILS,
     odor characteristic for each, See Table 7.

B.P. 188–190 ....AMYL VALERATE.
     Specific gravity 0.880 at 15° C.   Strong apple odor.
Saponified by boiling potassium hydroxide and acidified
yields valeric acid and amylic alcohol, which see.

B.P. 155 under 20 mm. pressure.   C, 69.42%; H,
     10.74%; O, 19.84%....................CORYFIN.
     Difficultly soluble in water, soluble in organic solvents.
Saponified with KOH solution yields menthol and ethyl
glycollic acid.

2. Crystalline Solids.

Melting-Point 22.   C, 81.08%; H, 8.20%; O, 10.72%.
                         ANETHOL (Anise camphor).
     Insoluble in water, soluble in common organic solvents.
B.P. 234.

M.P. 30.   C, 64.86%; H, 6.48%; O, 28.76%.
                         APIOL (Parsley camphor).
     White needles, insoluble in water, soluble in alcohol and
ether, characteristic faint odor, B.P. 294.   Strong sulphuric
acid gives a blood red color.   Saponified with caustic potash
isoapiol, M.P. 56 is formed.   Oxidized by potassic per-
manganate, apiolic acid, M.P. 176, is formed.

M.P. 40.   C, 56.03%; H, 3.92%; O, 12.47%.
                         MONOCHLORPHENOL.

M.P. 42–43.   C, 76.91%; H, 12.87%; O, 10.28%.
                         MENTHOL.
     When triturated with camphor, thymol, etc., liquefaction
occurs.   Characteristic odor.   Left rotary.   No color with

sulphuric acid or ferric chloride. Soluble in common organic solvents.

M.P. 48. C, 61.85%; H, 5.15%; O, 33.00%.
    METHYLASPARIN (Acetyl salicylic methyl ester).

Boiled with water saponification occurs with the odor of methyl salicylate (wintergreen) and on now adding ferric chloride a violet color is produced. Insoluble in water, soluble in common organic solvents.

M.P. 49. C, 22.13%; H, 3.08%; Cl, 64.94%; O, 9.85% . . . . . . ISOPRAL (Trichlor isopropyl alcohol).

Prismatic crystals, camphoraceous odor and pungent taste followed by local anæsthesia. Soluble in water and organic solvents. When warmed with potassium hydroxide no odor of chloroform occurs.

M.P. 67. C, 73.99%; H, 4.11%; O, 21.90%.COUMARIN.

Insoluble in water, soluble in organic solvents. Characteristic sweet-clover odor.

M.P. 68. C, 36.37%; H, 1.53%; O, 8.22%; Cl, 53.88%.
    TRICHLORPHENOL.

M.P. 74. C, 54.96%; H, 9.93%; N, 10.69%; O, 24.42% . . . . . . HEDONAL (methyl propyl carbinol).

White crystalline powder. B.P. 215. Difficultly soluble in water but easily soluble in organic solvents. Decomposed by boiling with potassium hydroxide solution.

M.P. 76. C, 51.95%; H, 6.49%; Br, 34.63%; O, 6.93% . . . . MONOBROMATED CAMPHOR.

White crystals. Saponified by potassium hydroxide and an excess of nitric acid added, silver nitrate (after filtering) gives a yellowish white precipitate of silver bromide difficultly soluble in ammonium hydroxide. Sulphuric acid and ferric chloride give no color reactions. Soluble in organic solvents.

M.P. 80.   C, 93.75%; H, 6.25%; O, 00.00%.

<div align="right">NAPHTHALENE.</div>

No color reactions if pure with sulphuric acid or with ferric chloride.   Specific gravity 1.152.   Insoluble in water but soluble in organic solvents.   Alcoholic solution heated with picric acid solution gives on cooling golden yellow needles of the picrate.

M.P. 80–81.   C, 63.15%; H, 5.35%; O, 31.52%.

<div align="right">VANILLIN.</div>

Ferric chloride gives a blue color with the solution, which turns brown on boiling.   A white precipitate on cooling strongly.   Difficultly soluble in water but soluble in organic solvents.   Extracted from organic solutions by ammonium hydroxide or by sodium bisulphite.   Characteristic vanilla odor.

M.P. 82.   C, 27.12%; H, 3.99%; Cl, 59.79%; O, 9.10% ......CHLORETONE (Chlorbutanol acetone).

Soluble in water and in most organic solvents.

M.P. 95.   C, 21.75%; H, 0.91%; Br, 72.50%; O, 4.84%.....................,..TRIBROMPHENOL.

Saponified with KOH solution and an excess of nitric acid added, the solution gives a pale yellowish white precipitate with silver nitrate which is difficultly soluble in ammonium hydroxide.   Ferric chloride gives a violet color.   Soluble in organic solvents.

M.P. 115.   C, 3.04%; H, 0.25%; I, 96.67%..IODOFORM.

Saponified by KOH solution and an excess of nitric acid added, silver nitrate gives a yellowish white precipitate of silver iodide, and a blue color with starch paper.   Sulphuric acid and ferric chloride give no color reactions.   Odor characteristic.   Soluble in most organic solvents.

M.P. 167.   C, 15.43%; H, 2.25%; Br, 77.17%; O, 5.15%.............................BROMETONE.

Slightly soluble in water.   Soluble in all organic solvents.

M.P. 175.   C, 78.94%; H, 10.52%; O, 10.54%.

<div align="right">CAMPHOR.</div>

Characteristic odor.   Optically active.   Insoluble in water. Soluble in all common organic solvents.   Liquefies with thymol.   Sulphuric acid and ferric chloride give no color reactions.

M.P. 203–205.   C, 71.42%; H, 9.53%; O, 19.05%.

<div align="right">OXAPHOR (Oxycamphor).</div>

White crystalline powder, difficultly soluble in water but soluble in all common organic solvents.

B. NOT EXTRACTED BY ETHER

B. *Separated along with the dissolved ether through a distilling tube from the water solution.*

B.P. 56.5.   C, 61.90%; H, 10.40%; O, 27.70%.

<div align="right">ACETONE.</div>

Specific gravity 0.790 at 25° C.   Soluble in water and organic solvents.   Warmed with potassic iodide and iodine yields iodoform, even in the cold.   With sodium nitroprusside and potassium hydroxide, is given a red or reddish yellow color passing to yellow, and on the addition of acetic acid becoming carmine red, purple red, and on warming violet.

B.P. 66.   C. 37.46%; H, 12.58%; O, 49.96%.

<div align="right">METHYL ALCOHOL.</div>

Specific gravity 0.815.   Oxidized by a glowing hot spiral or roll of oxidized copper gauze it gives tests for formic aldehyde, e.g., a red zone at the point of contact of the liquid flowed over sulphuric acid containing a little salicylic acid.

B.P. 78.   C, 76.52%; H, 6.43%; O, 17.05%.

<div align="right">ETHYL ALCOHOL.</div>

Specific gravity 0.816 at 15.5° C.   Warmed with iodine, potassium iodide and potassium hydroxide iodoform is formed. Heated with benzoyl chloride and agitated with KOH solution, the characteristic odor and reactions of ethyl benzoate appear.   Heated with potassium dichromate and

sulphuric acid, the characteristic odor of aldehyde is produced with the reduction of a green precipitate from the chromium. Heated with sodium or potassium acetate and sulphuric acid, the characteristic odor of ethyl acetate (acetic ether) is produced. On being allowed to stand with KOH solution and carbon disulphide, and some ammonium molybdate and dilute sulphuric acid afterward added, a red color is produced. For calculating the quantity from the specific gravity of the aqueous solution see Table 5.

B. *Not distilled from the water through the distilling tube, but if desired may be again distilled with steam.*

SOLIDS

M.P. 44. (See below) . . . . PIPERAZINE (Hydrated).

M.P. 49.   C, 22.13%; H, 3.08%; Cl, 64.94%; O, 9.85% ISOPRAL (Trichlor isobutyl alcohol).

Prismatic crystals with a camphoraceous odor, and pungent taste followed by some anesthesia of the tongue. Hypnotic. Soluble in water and organic solvents. When saponified with KOH solution no chloroform results.

M.P. 53.5.   C, 5.82%; H, 1.45%; Br, 77.18%; O, 15.15% . . . . BROMAL HYDRATE.

Reactions similar to those of chloral except in test for bromine.

M.P. 58.   C, 14.57%; H, 1.82%; Cl, 64.15%; O, 19.46% . . . . HYDRATED CHLORAL.

Soluble in water and organic solvents. Heated with magnesium hydroxide and water it yields chloroform (see tests) and formic acid (in filtrate from the excess of magnesia). Heated with mercuric chloride or silver nitrate, reduction occurs. With Nessler's reagent a brick red precipitate occurs which passes into a dirty yellowish green.

M.P. 78.   C, 24.53%; H, 3.57%; Cl, 53.98%; O, 17.92% . . . . CROTON CHLORAL (Butyl chloral).

Soluble in water and organic solvents. Heated with

magnesium hydroxide and water it yields formic acid, magnesium chloride and dichlorpropylene.

M.P. 80–100 (decomposed)................BORIC ACID.

Burned with alcohol it yields a characteristic green flame and spectrum. Soluble in water and alcohol.

M.P. 104 (also see 44). C, 55.81%; H, 11.70%; O, 32.49%...........................PIPERAZINE.

Generally contains six or more molecules of water of crystallization. Hygroscopic crystals soluble in water and alcohol. Strongly alkaline and forms salts with acids. Yields precipitates with several alkaloidal reagents; that with potassium bismuth iodide being scarlet red. White precipitate with Nessler's reagent. Blue precipitate with cupric sulphate.

LIQUIDS.

Boiling-Point 21. C, 40.00%; H, 6.66%; O, 53.34%. FORMALDEHYDE.

Gas occurring in aqueous solution. Odor and taste pungent and stinging. Soluble in water and alcohol. Dilute solutions floated over sulphuric acid containing some salicylic acid give a deep red zone. Warmed with silver nitrate, mercuric chloride or gold chloride, a reduction occurs with the formation of a mirror in the first instance if ammoniacal silver nitrate be used. Precipitates gelatin, albumens and tannins from their solutions.

B.P. 25. C, 44.37%; H, 3.72%; N, 51.01%. HYDROCYANIC ACID.

Characteristic peach kernel odor. Unstable. Precipitated by silver nitrate. With ferric chloride and ferrous sulphate and potassium hydroxide, it yields Prussian blue on the addition of hydrochloric acid. With ammonium sulphide and a trace of sodium hydroxide, it yields on evaporating and treating with water, hydrochloric acid and a little ferric chloride, a blood red color due to ferric sulphocyanide.

B.P. 101, M.P. 8.6.   C, 26.07%; H, 4.38%; O, 69.55%.

FORMIC ACID.

The neutralized solutions give a blood red color with ferric chloride and a reddish brown precipitate on boiling.   With basic lead acetate and alcohol it yields a *crystalline* precipitate. With silver nitrate it yields first a precipitate and finally a reduction of metallic silver.   Similar reactions with gold chloride and mercuric chloride.

B.P. 118, M.P. 17.   C, 40.00%; H, 6.67%; O, 53.33%.

ACETIC ACID.

Strong vinegar odor and taste, when neutralized by alkalies the salts give blood red precipitates with ferric chloride which becomes brown on boiling.   Heated with sulphuric acid and alcohol the characteristic odor of ethyl acetate is produced.

B.P. 190.   C, 18.75%; H, 1.56%; Cl, 54.69%; O, 25.00%..................DICHLORACETIC ACID.

B.P. 290.   C, 39.13%; H, 8.70%; O, 52.17%.

GLYCERIN.

Soluble in water and alcohol.   Insoluble in ether, chloroform, benzene and petroleum ether.   With a borax bead it gives a green boric acid flame and spectrum.

II. INSOLUBLE IN WATER OR READILY CRYSTALLIZING THEREFROM ON COOLING. SOLUBLE IN ORGANIC SOLVENTS

A. CRYSTALLINE

Thick liquid.   C, 65%; H, 5%; O, 30%.

CREOSOTE CARBONATE.

On cooling deposits mass of white crystals.   No color reaction with ferric chloride.   Saponified with KOH solution it yields creosote.

Thick liquid.   C, 74.45%; H, 8.03%; O, 17.52%.

SALIT (Borneol salicylic ester).

Saponified with alcoholic KOH solution it yields borneol and salicylic acid (which see).   Deposits crystals on cooling.

Thick liquid. C, 75%; H, 11.70%; O, 13.30%.

VALIDOL.

Methol ester of valeric acid mixed with free menthol. Saponified with alcoholic KOH solution and diluted with water menthol is liberated, and on acidifying with sulphuric acid valeric acid is also set free.   Crystals on cooling, strongly. ·

Thick Oily Liquid. C, 64.51%; H, 6.46%; O, 29.03%.

MONOTAL (Methylglycollic ester of guaiacol).

Saponified with alcoholic KOH, glycollic acid and guaiacol are liberated.   Deposits crystals on cooling strongly.

Thick Oily Liquid. C, 59.29%; H, 5.49%; O, 35.22%.

MESOTAN.

Methyloxymethyl ester of salicylic acid.   Above 100° C. it decomposes into salicylic acid, methyl alcohol and formic aldehyde.   Ferric chloride gives a violet color.   Sulphuric acid a red one.

Oily Liquid. C, 15.86%; H, 2.22%; N, 18.50%; O, 63.42%.................GLYCERYL TRINITRATE.

When freed from its usual alcoholic solvent or inert filling materials it explodes violently on heating or percussion. Decomposed by saponifying with KOH solution into potassium nitrate and glycerin.   Specific gravity 1.60.

M.P. 30. C, 64.86%; H, 6.48%; O, 28.66%...APIOL.

Characteristic faint odor, B.P. 290° C.   Blood-red color with sulphuric acid.   Yields isoapiol on saponifying, M.P. 56. Heated with potassium permanganate it yields apiolic acid, M.P. 175.

M.P. 36.6. C, 60.00%; H, 4.45%; O, 35.55%.

ACETOZONE (Benzoyl acetyl peroxide).

White shining crystals which liberate oxygen easily.

M.P. 42–43. C, 76.91%; H 12.17%; O, 10.28%.

MENTHOL.

Triturated with camphor, thymol, etc., it liquefies. Optical rotation left. No reactions with ferric chloride or sulphuric acid. Characteristic peppermint odor.

M.P. 42–43. C, 72.89%; H, 4.67%; O, 22.44%..SALOL.

On saponifying with KOH solution and adding an excess of hydrochloric acid, salicylic acid and phenol are liberated (which see). Violet color with ferric chloride. Bromine water causes a white precipitate. No color with sulphuric acid.

M.P. 50–51. C, 80.00%; H, 9.33%; O, 10.67%.

THYMOL.

Liquefies when triturated with camphor, menthol, etc. Sulphuric and nitric acids added to the acetic acid solution produce a bluish-green color. Heated with KOH solution and some chloroform added, a violet color is produced. No reactions with sulphuric acid or ferric chloride.

M.P., 50–51. C, 65.45%; H, 6.66%; N, 8.48%; O, 19.41%............................EUPHORIN.

(Phenyl carbamic acid ethyl ester).

White needles. Aromatic clove-like odor.

M.P. 56–69. C, 76.05%; H, 12.69%, O; 11.26%.

Pure STEARIC ACID.

Boiled with KOH solution it yields soft soap.

M.P. 59. C, 70.13%; H, 9.09%; 30.78%..CAPSICIN.

Soluble in KOH solution. Yields crystalline compounds with calcium, mercury and lead salts.

M.P. 61. C, 15.89%; H, 1.99%; N, 18.54%; O, 63.58%.............ERYTHROL TETRANITRATE.

Explodes on percussion and on heating when separated from solvents or diluents. Saponified by KOH solution it yields potassium nitrite and erythrol.

M.P. 65.   C, 68.85%; H, 4.92%; O, 26.23%.

GUAIACOL SALOL.

On saponification yields salicylic acid and guaiacol (which see).   Ferric chloride gives a wine red color.

M.P. 76.   C, 51.95%;   H, 6.49%;   Br, 34.63%;   O, 6.93% . . . . MONOBROMATED CAMPHOR.

On saponification with KOH and adding an excess of nitric acid it yields silver bromide with silver nitrate.   No color reactions with sulphuric acid or ferric chloride.

M.P. 74–76.   C, 61.53%; H, 11.11%; O, 27.36%.

HEDONAL (Methyl propyl carbinol urethane).

M.P. 76.   C, 39.67%;   H, 7.43%;   S, 26.44%;   O, 26.44% . . . . TRIONAL.

Melted with potassium hydroxide it yields the odor of mercaptan on dissolving in water, and a blue color becoming violet on adding an excess of hydrochloric acid, and yielding then an odor of sulphur dioxide.   No color reactions with sulphuric acid or ferric chloride.

M.P. 80.   C, 93.75%; H, 6.25%; O, —.——.

NAPHTHALENE.

No reactions with ferric chloride or sulphuric acid.   Characteristic odor.

M.P. 83.   C, 71.42%; H, 9.52%; O, 19.06%.

BAROSMA CAMPHOR (diosphenol).

Solutions in KOH are precipitated by carbon dioxide. Ferric chloride gives a blackish green color.   No color with sulphuric acid.

M.P. 85–87.   C, 65.69%; H, 5.11%; O, 29.20%.

GUAIACOL CARBONATE.

Saponified with KOH solution and acidified it yields guaiacol (which see) (blue color with ferric chloride).   With the original substance ferric chloride and sulphuric acid produce no color unless impure.

M.P. 86–88. C, 62.15%; H, 6.78%; N, 8.97%; O, 22.10%........THERMODIN (Phenacetin urethane).

Warmed with sulphuric acid and alcohol an ethyl acetate odor is produced. With sulphuric acid and sugar a red color becoming more distinct on standing (diff. from neurodin).

M.P. 87–88. C, 66.08%; H, 6.66%; N, 4.06%; O, 23.20%............................EUPYRINE.

Light yellow needles. Sulphuric acid gives a greenish-yellow color becoming dark brown on warming. Decomposed by acids and alkalies with a faint odor of vanilla.

M.P. 89. C, 48.20%; H, 8.93%; S, 14.27%; O, 28.60%............................TETRONAL.

Melted with KOH an odor of mercaptan becomes pronounced on dissolving in water, with the production of a bluish color, which on supersaturating with hydrochloric acid becomes violet with the liberation of sulphur dioxide.

M.P. 95. C, 77.27%; H, 4.54%; O, 18.19%.

BETOL (Naphthol salicylate).

Saponified with KOH solution it yields salicylic acid and naphthol. With sulphuric acid it gives a lemon yellow color which on addition of a trace of nitric acid becomes brownish green.

M.P. 95. C, 69.69%; H, 7.07%; N, 7.07%; O, 16.17%.

EUQUININE (Quinine ethylcarbonic ester).

White nearly tasteless needles. Forms bitter salts with acids. Gives thalleioquin test but no herapathite test. Warmed with potassium hydroxide and iodine solutions, iodoform is produced.

M.P. 104. C, 65.70%; H, 5.11%; O, 29.19%.

SANTALIN.

Reddish yellow crystals giving a deep red color with sulphuric acid and a violet one with alkalies.

M.P. 110. C, 75.00%; H, 8.33%; O, 16.67%.

HELENIN.

M.P. 113. C, 71.11%; H, 6.66%; N, 10.37%; O, 11.86%........................ACETANILIDE.

Boiled with KOH solution an odor of aniline becomes apparent and on the addition of chloroform and again heating the disagreeable odor of phenyl isonitrile. Boiled with hydrochloric acid it gives a brownish red color on the addition of a few drops of phenol and some calcium hypochlorite solution, which color becomes blue on the addition of an excess of ammonium hydroxide. Sulphuric acid and ferric chloride produce no colors.

M.P. 114. I, 100%.......................IODINE.

Soluble in potassium iodide solution and then colors starch blue. Solutions give a pale yellowish white precipitate with silver nitrate insoluble in ammonium hydroxide.

M.P. 115. C, 3.04%; H, 0.25%; I, 96.67%. IODOFORM.

Characteristic odor. Heated with alcoholic KOH solution and water and an excess of nitric acid added, the solution colors starch blue and gives with silver nitrate a pale yellowish white precipitate insoluble in ammonium hydroxide. Sulphuric acid and ferric chloride give no color reactions. Fine yellow micro-crystalline powder.

M.P. 115–118. S, 100%..................SULPHUR.

Dissolves by boiling with caustic alkalies. Burns with the evolution of sulphur dioxide odor.

M.P. 115 (decomposed). C, 18.78%; H, 2.02%; N, 7.30%; Cl, 55.11%; O, 16.73%..CHLORALAMID.

Decomposed by heat and alkalies into chloral and ammonium formate (which see).

M.P. 116–117. C, 63.15%; H, 11.57%; O, 25.28%. TERPIN HYDRATE.

Sulphuric acid gives an orange yellow color.

M.P. 117–118. C, 63.15%; H, 7.18%; N, 6.69%; O, 19.98% ... LACTOPHENIN (Para lactylphenetidin).

Boiled with ten parts of hydrochloric acid and 100 parts of water added, the filtrate gives with a few drops of chromic

acid solution a ruby red color. Aqueous solutions give an insoluble precipitate with bromine water. Boiled with hydrochloric acid and water for some time, the solution gives an indophenol reaction with phenol and calcium hypochlorite solution.

M.P. 120.   C, 68.04%; H, 8.24%; N, 7.21%; O, 16.51% . . . . . . TRIPHENIN (Propionylphenetidin).

Reactions and uses similar to those of phenacetin and lactophenin.

M.P. 121.   C, 68.85%; H, 4.91%; O, 26.24%.

BENZOIC ACID.

Neutralized with NaOH or KOH solution, ferric chloride gives a flesh colored precipitate. Sulphuric acid gives no color. Sublimes easily.

M.P. 121.5.   C, 17.38%; H, 1.03%; I, 78.26%; O, 3.33% . . . . LOSOPHAN.

M.P. 122.   C, 83.33%; H, 5.55%; O, 11.12%.

BETANAPHTHOL.

Bromine water gives white precipitate in solutions, soluble in ammonium hydroxide. Ammonium hydroxide gives a blue fluorescence. Sulphuric acid and ferric chloride give no color reactions.

M.P. 124.   C, 61.34%; H, 3.49%; O, 33.17%.
         C, 62.16%; H, 5.40%; O, 32.44%.

PODOPHYLLOTOXIN.

Often resinous. Ammonium hydroxide changes it to picropodophyllotoxin of the same composition. Potassium hydroxide produces a deep yellow color. Insoluble in petroleum ether, which precipitates it from the chloroform solution. Sulphuric acid produces a yellow color, changing to purplish and brown on the addition of nitric acid.

M.P. 125–126.   C, 36.84%; H, 7.01%; S, 28.07%; O, 28.08% . . . . SULFONAL.

Melted with KOH and the melt dissolved in water, the

disagreeable odor of mercaptan is apparent, also a blue color, which on the addition of an excess of hydrochloric acid changes to violet with the liberation of sulphur dioxide gas. Sulphuric acid and ferric chloride produce no color reactions.

M.P. 128. C, 67.42%; H, 5.62%; O, 26.96%.

CUBEBIN.

Sulphuric acid gives a red color. Bitter needles.

M.P. 133. C, 72.99%; H, 5.41%; O, 21.60%.

CINNAMIC ACID.

Oxidized with potassium permanganate in sulphuric acid solution it yields benzoic aldehyde (bitter almond odor). Manganous sulphate yields precipitates with salts (diff. from benzoates).

M.P. 135. C, 60.00%; H, 4.44%; O, 35.56%.

ASPIRIN (Acetylsalicylic acid).

Saponified with KOH solution and neutralized by acid, it yields a violet color with ferric chloride (salicylic acid), and the distillate after acidification, reacts for acetic acid.

M.P. 135. C, 67.04; H, 7.25%; N, 7.82%; O, 17.80%.

PHENACETIN.

No color reactions with sulphuric acid or ferric chloride. Solutions (aqueous) give a white precipitate with bromine water. Boiled with ten parts of hydrochloric acid and one hundred parts of water added, the filtrate on the addition of a few drops of chromic acid solution gives a ruby red color.

M.P. 141. C, 65.26%; H, 6.66%; O, 28.08%.

CUSSIN.

M.P. 141–143. C, 57.49%; H, 5.40%; N, 8.39%; O, 28.72%.   ORTHOFORM (New),

(Methyl ester of meta amidoparaoxy-benzoic acid).

Tasteless. Sometimes crystallizes from chloroform with a M.P. of 110–111 due to chloroform of crystallization. Ferric chloride gives a fugitive color; with water, hydrochloric acid

and sodic nitrate a yellowish red to red precipitate. Ortho-
form (new) hydrochloride is soluble in water.

M.P. 140–150 (decomposed). C, 8.40%; H, 0.19%;
    I, 88.96%; N, 2.45%.....................Iodol.

Sulphuric acid gives a green brown color. Pale yellow,
light, microcrystalline powder.

M.P. 146. C, 32.30%; H, 5.10%; Br, 35.90%; O,
    14.20%.   Bromural.
           (Alpha monobromisovalerylurea).

Heated with potassium hydroxide solution, it then gives
nitrogen gas with sodium hypobromite solution.

M.P. 151. C, 72.31%; H, 5.22%; O, 22.47%.
                                      Chrysarobin.

Yellowish powder. With potassium hydroxide it becomes
deep yellow, red, green with fluorescence. Sulphuric acid is
colored yellow, becoming red on dilution with water, the color
being restored. Color with ferric chloride reddish brown.
Nitric acid gives a red color becoming violet on the addition
of ammonium hydroxide. Calcium hydroxide solution gives
a violet color. Sulphuric acid with a little potassium dichro-
mate gives a red changing to green and finally to purple and
brown.

M.P. 151. C, 56.99%; H, 3.60%; O, 39.41%.
          Novaspirin (Methylenecitrylsalicylic acid).

M.P. 152. C, 62.50; H, 4.16%; O, 33.34%. Anemonin.

M.P. 157. C, 60.87%; H, 4.34%; O, 34.79%.
                             Salicylic Acid.

Ferric chloride gives a deep blue violet color. Sulphuric
acid gives none. Heated with sulphuric acid and methyl
alcohol, the characteristic odor of methyl salicylate is produced.

M.P. 165. C, 57.14; H, 4.78%; O, 38.10%.
              Lenigallol (Triacetylpyrogallol).

M.P. 165–167. C, 68.25%; H, 5.70%; O, 26.05%.
                              Curcumin.

Vanilla-like odor. Gives a red brown color with KOH.

Oxidized to vanillin by potassium permanganate (which see). Boiled with sulphuric acid it yields rosocyan (red) soluble in alcohol but insoluble in water, which warmed with KOH becomes blood red and finally yellow.

M.P. 167. C, 15.43%; H, 2.25%; Br, 77.17%; O, 5.15% . . . . BROMETONE.

Reactions like those of chloretone except for the presence of bromine.

M.P. 170. C, 73.17%; H, 7.32%; O, 19.51%.

SANTONIN.

Sulphuric acid is colored from white to yellowish or reddish. A red color is produced by boiling with alcoholic KOH solution. Boiled with water containing a little sulphuric acid, it gives a violet color with ferric chloride.

M.P. 170–175 (also 177–178). C, 35.40%; H, 1.64%; N, 4.59%; Cl, 11.53%; I, 41.64%; O, 6.20%.

VIOFORM (Iodochloroxyquinoline).

Millon's reagent gives a green color, ferric chloride a green, and sulphuric acid a brown. With chloroform and nitric acid a violet red and sometimes yellow.

M.P. 175. C, 78.94%; H, 10.52%; O, 10.52%.

CAMPHOR.

Liquefies when triturated with thymol, menthol, etc., sublimes readily, rotates the plane of polarized light to the right, and gives no color with sulphuric acid or ferric chloride.

M.P. 175–178. C, 63.53%; H, 3.54%; O, 32.93%.

PURGATIN (Diacetyl ester of trihydroxyanthraquinone).

Orange colored microcrystalline powder. Soluble in alkalies with a deep violet red color.

M.P. 180–190. Composition somewhat variable.

EXODIN.

A mixture of derivatives from rufigallic acid. Greenish yellow powder.

M.P. 184.   C, 81.55%; H, 10.68%; O, 7.77%.

LACTUCERIN (Lactucon).

Saponified with alcoholic KOH solution it yields acetic acid (volatile and in solution) and lactucol, M.P. 154-155 (insoluble)   No color reactions with sulphuric acid or ferric chloride.

M.P. 184. • C, 60.00%; H, 8.00%; O, 32.00%.

CAMPHORIC ACID.

Rotates the plane of polarized light 48 degrees to the right.

M.P. 187-188.   C, 68.57%; H, 5.30%; O, 26.13%.

SALOPHEN (1-4 acetamidophenol salicylic ester). Insoluble in petroleum ether.

M.P. 189.   C, 72.99%, H, 6.83%; N, 8.31%; O, 11.87% . . . ARISTOCHIN (Quinine carbonic ester).

Combines with one and two molecules of hydrochloric acid to form salts.   Decomposed by acids and alkalies with liberation of quinine.

M.P. 190-195 (also 166).   C, 73.46%; H, 4.76%; O, 21.78%.

EPICARIN (Oxynaphthyl ortho-oxytoluylic acid).

Ferric chloride gives a deep blue color.   Warmed with sulphuric acid gives a red brown solution with green fluorescence.   Shaken with NaOH or KOH solution and chloroform a yellow to yellowish green solution results (diff. from betanaphthol) which is deep blue.   Solutions are precipitated by lead acetate.

M.P. 191.   C, 52.17%; H, 6.53%; N, 15.23%; O, 26.08%. . . . . VERONAL (Diethylbarbituric acid).

Forms easily soluble alkaline salts.   Not precipitated by lead salts.   Difficultly soluble in chloroform, insoluble in benzene and petroleum ether.

M.P. 191-200.   C, 69.46%; H, 5.27%; O, 25.27%.

ROTTLERIN.

Yellow silky needles from Kamala.   Unstable in the air. Analyses also give C, 71.00%; H, 10.05%; O, 18.95%.

M.P. 200. C, 60.50%; H, 5.88%; O, 33.62%.

PICROTOXIN.

Sulphuric acid is colored golden yellow, red and finally brown. Treated with a mixture of sulphuric and nitric acids and then an excess of sodium hydroxide added, it assumes a brick red color.

M.P. 204–205. C, 60.96%; H, 4.81%; O, 34.25%.

CATECHIN.

M.P. 211–213. C, 61.22%; H, 6.13%; O, 32.65%.

FORTOIN (Cotoin formaldehyde).

Yellowish needles, difficultly soluble in alcohol ether and benzene but readily soluble in chloroform, acetone, and alkalies. Sulphuric acid produces an orange color becoming ruby red on warming.

M.P. 216. C, 68.86%; H, 8.10%; O, 23.04%.

ELATERIN.

Sulphuric acid gives a yellow color becoming scarlet red. Sulphuric acid with potassium dichromate gives an olive green to dark green. Sulphuric acid with vanadium oxide gives a blue, green and dark green, and finally brown color. Evaporated with hydrochloric acid, the residue washed with water and treated with sulphuric acid gives a brownish red color.

M.P. 218. C, 64.51%; H, 6.45%; O, 29.04%.

CANTHARIDIN.

Extracted by caustic alkalies from organic solvents. Sodium salts precipitated by lead acetate, barium chloride, and mercuric chloride; 0.0001 gramme will blister.

M.P. 240 (softens 150). C, 54.92%; H, 5.63%; O, 39.45% . . . . BAPTISIN.

M.P. 250. C, 75.78%; H, 7.37%; O, 16.85%.

HELLEBORIN.

M.P. 250–253. C, 75.47%; H, 4.41%; O, 20.12%.

PHENOLPHTHALEIN.

Colorless with acids, deep red with alkalies.

M.P. 253.   C, 65.62%; H, 4.76%; O, 38.11%.

PURPURIN.

Orange yellow needles. Red violet color with KOH solution. Distilled with zinc dust it yields anthracene. With nitric acid it yields phthalic acid. Soluble in alum solution.

M.P. 290 (also 215).   C, 70.00%; H, 3.33%; O, 26.67%.

ALIZARIN.

Red brown needles. Violet color with KOH solution, precipitated by carbon dioxide. Precipitated by calcium chloride, barium chloride and most heavy and alkaline earth metals.

M.P. 390-392.   C, 73.28%; H, 3.82%; N, 10.68%; O, 12.22% . . . . INDIGOTIN (Indigo blue).

B   AMORPHOUS

Melting Points Indefinite or the Bodies Decomposed by Heat

M.P. ——.   C, 53.88%; H, 3.80%; N, 5.06%; O, 37.26% . . . . TANNOPIN

(Hexamethylene tetramine tannin).

Heated with water and sulphuric acid it yields formaldehyde. Heated with water and KOH solution it yields ammonia, and the residue contains decomposition products of tannin.

M.P. ——.   C, 53.04%; H, 3.05%; O, 43.91%.

TANNOFORM (Tannin formaldehyde).

Soluble in alkalies. Warmed with sulphuric acid it produces a brown, green, blue, and after adding alcohol a more brilliant blue, changing to wine color and on the addition of KOH solution pale green.

C, 53.20%; H, 3.45%; O, 43.35%.

TANNIGEN (Diacetyl tannin).

Dissolves in dilute KOH solution, which then becomes gelatinous on adding an excess of acetic acid and gives a greenish black color with ferric chloride.

XEROFORM (Tribromphenol bismuth).

Decomposed into its constituents (which see) by alkalies.

M.P. ——. C, 41.09%; H, 4.10%; I, 45.98%; O, 8.83%...........................THYMOL IODIDE.

Fused with KOH and the cooled melt dissolved and an excess of nitric acid added, silver nitrate gives a pale yellowish white precipitate, insoluble in ammonium hydroxide.

M.P. ——. C, 66.08%; H, 6.08%; N, 8.11%; Mg, 3.47%; O, 16.26% ....CHLOROPHYLL.

Soluble in alcohol and acetone, difficultly soluble in ether Gives a characteristic spectrum. Present in all green plants.

M.P. ——. C, 76.59%; H, 12.06%; O, 11.35%.

OLEIC ACID.

Oily liquid. Forms soap with alkalies.

M.P. ——. Phosphorus 3.8 to 4.2%; N, 1.7% to 1.8%.

LECITHIN (Oleic, palmitic and stearic acid esters of glycerophosphoric acid).

Yellowish brown waxy-looking solid, soluble in alcohol, etc. Swells with water, decomposed by alkalies. Alcoholic solutions are precipitated by platinum chloride.

M.P. ——. C, 80.25%; H, 9.56%; O, 10.19%.

CANNABINOL.

Thick liquid B.P 265 under 20 mm. pressure. The active constituent of the resin of Cannabis and always associated with a terpene B.P. 160–180 under atmospheric pressure, a sesquiterpene B.P 258, and solid paraffin M.P. 63.64.

BROMIPIN.

A 10% addition product of bromine and sesame oil, the halogen being entirely added to the oil molecule.

IODIPIN.

A 10% addition product of iodine and sesame oil, the halogen being entirely added to the oil molecule.

PHLOBAPHENES.

Mostly reddish or brownish bodies associated with the tannins, which are soluble in ammonia, but insoluble in most organic solvents.

VARIOUS RESINS.

See Table 10 for physical and chemical properties.

VARIOUS FIXED OILS, FATS AND WAXES.

See Table 6 for physical and chemical properties.

M.P. 150–155. C, 55.10%; H, 8.10%; O, 36.74%
(impure) ....CONVOLVULIN.

Sulphuric acid gives a red color. Bromine water gives a
white precipitate. Reduces ammonio silver nitrate solution
directly but Fehling's solution only after hydrolysis with
dilute acids. Boiled with barium hydroxide it yields purginic
acid and convolvulinic acid, both soluble in water Purginic
acid, after hydrolysis by boiling with dilute acids, yields
glucose and convolvulinic acid, M.P 51.5. From Jalap
root.

M.P. 131. C, 56.66%; H, 7.77%; O, 35.57%. (impure)
JALAPIN.

Sulphuric acid gives a purple color changing to red.
Saponified by boiling with barium hydroxide it yields jalapinic
acid (soluble in water, diff. sol. in ether, precipitated by
barium chloride). Hydrolyzed with dilute hydrochloric acid
it yields jalapinolic acid, M P. 62.5 and glucose. From
Scammony, etc.

III. SOLUBLE IN WATER

A SOLUTIONS PRECIPITATED BY NEUTRAL LEAD ACETATE EX-
TRACTED BY ORGANIC SOLVENTS

M.P. 18. C, 40.00%; H, 6.66%; O, 53.34%.

LACTIC ACID.

Soluble in alcohol, water and ether Insoluble in chloro-
form, benzene and petroleum ether. Heated with potassium
permanganate an odor of aldehyde is produced.

M.P. 80–81. C, 63.15%; H, 5.33%; O, 31.52%.

VANILLIN.

Ferric chloride gives a blue color Characteristic odor
Extracted from immiscible solvents by ammonium hydroxide,
and liberated by acids.

M.P. 98 (with water of crystallization).
   Dry.   C, 26.66%; H, 2.23%; O, 71.11%.

<div align="right">OXALIC ACID.</div>

Calcium chloride gives precipitates insoluble in acetic acid but soluble in mineral acids.

M.P. 100–132.   C, 35.82%; H, 4.48%; O, 59.70%.

<div align="right">MALIC ACID.</div>

Needles of four- or six-sided prisms.   Heated to 175–180 it evolves maleic acid (M.P. 130, and vaporizes at 160), and fumaric acid (vaporizes at 200), both condense in needles. Not precipitated by calcium chloride from neutral salts (diff. from citric) unless quite concentrated

M.P. 100–140.   C, 63.57%; H, 4.63%; O, 31.79%.

<div align="right">HEMATOXYLIN.</div>

Sweet taste, red on exposure to light, precipitated by gelatin, barium hydroxide, cupric sulphate, gives a white gray precipitate becoming finally blue. Ammonium hydroxide gives a rose red color, becoming purple, black and finally blackish red Aluminum sulphate gives a deep violet colored precipitate. Soluble in water, alcohol and ether.

M.P. 103–107.   C, ——— .... COLALIN.
   (Bile acids mixed with magnesium carbonate).
Slightly soluble in water, soluble in alcohol.

M.P. 104.   C, 65.45%; H, 5.46%; O, 29.09%.

<div align="right">CATECHOL.</div>

Ferric chloride gives an emerald green color and precipitate, sodium bicarbonate a violet red, and NaOH a brownish black.   Reduces silver nitrate solution and Fehling's solution on warming.

M.P. 104.   C, 65.70%; H, 5.11%; O, 29.19%.

<div align="right">SANTALIN.</div>

Difficultly soluble in water when alone.   Soluble in alcohol and ether (red yellow) and in sulphuric acid (deep red), and in alkalies (violet).

M.P. 120. C, 45.90%; H, 2.73%; N, 7.65%; O, 26.24% ....SACCHARIN.

Difficultly soluble in water, soluble in dilute alkalies. Very sweet taste.

M.P. 120 (decomp.). C, 42.00%; H, 2.00%; O, 56.00% ....MECONIC ACID.

Ferric chloride gives a deep red color which is not changed by hydrochloric acid (formic and acetic acids) nor by mercuric chloride or gold chloride (sulphocyanides). Micaceous scales.

M.P. 125. C, 62.69%; H, 6.26%; O, 31 05%.

 185. C, 63.63%; H, 6.06%; O, 30.31%.

FILICIC ACID.

M.P. 127 (softens at 115). C, 34.28%; H, 4.77%; O, 60.95% ....ALPHOZONE

Light white microcrystalline powder, or plates Decomposes on standing with water liberating oxygen. Soluble in alcohol and ether, insoluble in chloroform, benzene and petroleum ether. Explodes in flame.

M.P. 130. C, 69.84%; H, 4.76%; O, 25.39% ..COTOIN.

M.P. 131. (sublimes) C, 57.13%; H, 4.77%; O, 38.10% ....PYROGALLOL.

Reduces salts of silver, mercury, gold, etc., in the cold. Ferric chloride gives a brownish red color and on the further addition of ammonium hydroxide a deep blue black. Solutions darken on exposure to the air, especially if alkaline. Soluble in alcohol and ether.

M.P. 135–137. C, 60.00%; H, 4.45%; O, 35.55%.

ASPIRIN.

Colorless needles, soluble in alcohol and ether With potassium hydroxide or sulphuric acid it yields salicylic acid and acetic acid. No color with ferric chloride.

M.P. 135. C, 32.00%; H, 4.00%; O, 64.00%.

TARTARIC ACID.

Soluble in water, alcohol, and somewhat in ether Insoluble in chloroform, benzene or petroleum ether Rotates polarized light to right. Calcium chloride gives a precipitate in the cold (diff. from citric) in alkaline solution, which is soluble in acetic acid (diff. from oxalic). Potassium acetate gives a precipitate in concentrated solutions especially if alcohol be present. Not precipitated by calcium sulphate

M.P. 135–153. C, 37.50%; H, 4.17%; O, 58.33%.

CITRIC ACID.

Soluble in water and alcohol, difficultly in ether, and chloroform. Alkaline calcium chloride solution gives no precipitate in the cold but precipitates on heating, which precipitate is insoluble in caustic potash (diff. from tartaric, oxalic and malic acids).

M.P. 140. C, ——. . . . . AGARICIN.

White, amorphous or crystalline powder Swells and dissolves in hot water forming a foaming solution Soluble in alkalies. Salts are precipitated by barium chloride, etc.

M.P. 140. C, 41.38%; H, 3.45%; O, 55.17%.

ACONITIC ACID.

Neutral salts give precipitates with lead nitrate and silver nitrate. Ferric chloride gives a red brown color and precipitate.

M.P. 173–176. C, 55.90%; H, 4.55%; O, 39.75%.

QUERCITRIN.

By hydrolysis with acids it yields quercitrin M.P 250 and glucose. Soluble in water, alcohol and ether. Ferric chloride gives a dark-green color. With KOH solution it turns dark brown on exposure to air. Precipitated brick red by lead acetate.

M.P. 175–177. C, 62.90% H, 4.84%; O, 32.26%.

CATECHIN B.

Needle-like crystals, soluble in water, alcohol and ether Ferric chloride gives a green color and precipitate.

M.P. 175–177.   C, 60.43%; H, 8.37%; O, 31.20%.

PARILLIN.

By hydrolysis with acids, glucose and paragenin are formed.   Strong sulphuric acid gives a yellow, whiter and slowly red color.   Sulphuric acid with potassium dichromate gives a green color.   Precipitated by barium hydroxide, etc.

M.P. 185.   C, 62.68%; H, 6.26%; O, 31.06%.

FILICIC ACID (Crystals).

(See M P. 125)

M.P. 186–188.   C, 70.86%; H, 3.95%; O, 25.20%.

CHRYSOPHANIC ACID (Rhubarb).

By hydrolysis with dilute acids it yields glucose and emodin, M.P. 254.   KOH solution gives a deep red color. Barium hydroxide gives a red precipitate.

M.P. 200.   C, 62.17%; H, 8.81%; O, 29.02%.

GRATIOLIN.

M.P. 206–208.   Free C, 43.29%; H, 4.12%; O, 52.59%

CITARIN (Sodium anhydromethylenecitrate).

A 1% watery solution flowed over sulphuric acid containing 5% of sodium nitrate gives a blue contact ring.   Heated with KOH solution and resorcinol added, a red color and odor of formaldehyde result.   Insoluble in organic solvents but the free acid is soluble in these.

M.P. 222.   C, 49.41%; H, 3.53%; O, 47.06%.

GALLIC ACID.

Sulphuric acid gives no color or a pale brown, KOH solution a greenish, with hydrochloric acid a red or brownish red, with ammonium hydroxide a red.   Ferric chloride gives a bluish black.   No precipitate with albumen or gelatin (diff from tannins)

M.P. 235.   C, 59.80%; H, 5.64%; O, 34.56%.

ONONIN.

Glucoside.   By hydrolysis it yields glucose and formonetin.

M.P. 254.   C, 66.59%, H, 3.82%; O, 29.59%.

EMODIN.

  Reddish crystals, red precipitate with salts of the alkaline earths and many heavy metals.   With ammonium hydroxide (or KOH) it gives a characteristic red color and spectrum (Borntraeger's reaction).

M.P. 258-260.   C, 54.64%, H, 5.04%; O, 40.32%.

RUBERYTHRIC ACID (Madder).

M.P. 320.   C, 51.02%; H, 4.89%; O, 44.89%.

FRAXIN.

  Glucoside.   By hydrolysis with dilute acids it yields glucose and fraxetin M. P 227

M.P.——.   C, 67.13%; H, 4.89%; O, 27.98%.

BRAZILIN.

  Difficultly soluble in water   Colorless at first, reddened by light changing to brazilein.   Bright red by alkalies.

M.P.——.   C, 55.62%; H, 2.00%; O, 42.38%.

ELLAGIC ACID.

  Yellowish tasteless powder, insoluble in acid and neutral liquids but soluble in alkalies.   Ferric chloride gives a dark greenish black color.   Nitric acid gives a dark red color Difficultly soluble in ether, insoluble in benzene and petroleum ether

Free C, 33.80%; H, 3.28%; N, 6.56%; As, 35.21%; O, 21.15%.

Dry C, 36.18%, H, 3.01%; N, 7.03%; As, 37.70%; O, 16.08% . . . . ATOXYL

  Sodium salt of p-aminophenylarsenic acid, containing from two to four molecules of water on crystallization, and about 26% of arsenic.   No precipitate of arsenic with hydrogen sulphide in the cold, but precipitated on heating.   Hydrochloric acid and potassium iodide yield free iodine.   Very stable but decomposed by fusing with KOH.   No isonitrile reaction for aniline.   Millon's reagent gives a turbid violet color.   White crystals or crystalline powder.

Free C, 59.59%; H, 6.38%, S, 17.00%; O, 34.04%.

ICHTHYOL.

Ammonium (or sodium) salt of ichthyolsulphonic acid. Ferric chloride gives a violet to brown color Soluble in ether-alcohol but not completely soluble in either alone. Precipitated and decomposed by hydrochloric acid

M.P.——.   S, 15.00%; Ag, 30%.........ICHTHARGAN.

C, 52.86%; H, 4.85%, O, 42.29%..THUJIN.

Glucoside. Ferric chloride gives a dark greenish black color Green precipitate with barium hydroxide.

M·P ——.   C, 59.12%; H, 7.05%; N, 1.56%; O, 32.27%........................GLYCYRRHIZIN.

Sweet. Hot neutral solutions gelatinize on cooling. Easily soluble in ammonia and alkalies generally Insoluble in common organic solvents except alcohol (slightly)

M.P.——.   C, 54.54%; H, 7.18%; O, 38.28%.

QUILLAJIC ACID.

Glucoside. By hydrolysis yields glucose and sapogenin Sulphuric acid gives a red color Easily soluble in water and foams strongly on shaking. Soluble in alkalies and slightly in alcohol and chloroform. Insoluble in ether and benzene.

M.P.——.   C, 42.10%; H, 6.43%; O, 51.47%.

ARABIC ACID.

Soluble in water, precipitated by alcohol.

Composition somewhat variable, generally from C, 52.40%; H, 3.67%; O, 43.93% (Pyrogallol tannins), to C, 59.65%; H, 4.65%, O, 35.70% (Catechol tannins).

TANNINS.

M.P.——.   C, 52.17%; H, 3.10%, O, 44.73% (Nutgall tannin).

Ferric chloride gives a blue black color (pyrogallol tannins) or a dark greenish black color (catechol tannins), all precip-

itate albumen, gelatin and most alkaloids, and give precipitates with bromine water.

Here are also various unnamed plant acids, with often
boric, phosphoric, carbonic, sulphuric, and hydrochloric acids.

MISCELLANEOUS PLANT ACIDS.

SOLUBLE IN WATER

B PRECIPITATED BY BASIC LEAD ACETATE   EXTRACTED BY
ORGANIC SOLVENT

Crystalline

M.P. 110.   C, 65.45%, H, 5.45%; O, 29.10%.

RESORCINOL.

Ferric chloride gives a blue violet color   Boiled with
KOH solution and chloroform, a crimson color is produced
Hydrochloric acid gives a straw yellow.

M.P. 120–125.   C, 68.18%; H, 7.58%; O, 24.24%.

ABSINTHIN.

Glucoside.   Sulphuric acid gives a brownish red color,
becoming greenish blue with water, brownish red with KOH
solution, and yellowish green with hydrochloric acid.   Mercuric nitrate gives a precipitate and ammonio silver nitrate
is reduced, but Fehling's solution is not.

M.P. 147.   C, 40.00%; H, 3.33%, O, 56.65%.

CURACAO ALOIN OR BARBALOIN.

Sulphuric acid with potassium dichromate gives a green
color, passing to greenish purple and greenish yellow.   Bright
red with nitric acid, boiled with nitric acid an intense red,
Bromine in hydrobromic acid gives a precipitate.   Mercuric
nitrate gives a precipitate.   Precipitates are also given by
tannin.   Fehlings solution and gold chloride are reduced.
Potassium cyanide with KOH gives a blood red color.   Ferric
chloride gives a brownish green color.

C, 59.47%; H, 5.54%; O, 34.99%...SOCALOIN.

Sulphuric acid with potassium dichromate gives an olive
green color, changing to dark green and finally to blue.

Bromine water gives a pink gold chloride a carmine red changing to violet, and ferric chloride a brownish green .

M.P 160.   (See Aesculin).

M.P. 162.   C, 43.75%; H, 6.25%; O, 50.00%.

QUINIC ACID.

Heated with sulphuric acid and manganese dioxide it yields carbon dioxide, formic acid and quinone   Heated with KOH it yields protocatechuic acid.   Present in from 5 to 7% in the bark.

M.P. 181.5.   C, 52.44%; H, 6.42%; O, 41.14%.

VERBENALIN.

Soluble in water, alcohol and ethyl acetate, insoluble in other common organic solvents.   Glucoside, reduces Fehling's solution directly and strongly

M.P. 199–200.   C, 57.60%; H, 4.00%; O, 38.40%.

SCUTELLARIN.

Basic lead precipitate is red. Ferric chloride gives a green color becoming red on heating.   Bitter glucoside from various mints.

M.P. 200.   C, 52.39%; H, 4.78%; O, 42.83%.

DAPHNIN.

Glucoside, by hydrolysis it yields glucose and daphnetin M.P. 253–256.   KOH solution gives a golden yellow and ferric chloride a bluish color.   Fehling's solution and ammonio silver nitrate are reduced.

M.P. 203.   C, 60.00%; H, 8.33%; O, 31.66%.

BRYONIN.

Glucoside, by hydrolysis yields sugar and bryogenin M.P. 210.   Only precipitated well by ammonio lead acetate.

M.P. 204.   C, ——....................WISTARIN.

Glucoside. Soluble in alcohol, foams with water, diffi-cultly soluble in ether, soluble in chloroform.   Yellow with KOH solution, yellow changing to cherry red with sulphuric acid, and violet changing to brownish green with ferric chloride.

M.P. 205 (see also 160). C, 52.94%; H, 4.71%; O, 42.35% . . . . AESCULIN.

Sulphuric acid followed by calcium hypochlorite gives a bright violet color, nitric acid followed by KOH solution a red, and ferric chloride a green. Solutions give a yellow blue fluorescence. Glucoside, yielding by hydrolysis sugar and aesculetin, M.P. 270.

M.P. 210. C, 59.62%; H, 5.59; O, 34.79%.

NATALOIN.

Sulphuric acid followed by nitric acid gives a blue color. Sulphuric acid with potassium dichromate a green, greenish purple and finally greenish yellow color. Nitric acid gives a brick red. Bromine in hydrobromic acid, mercuric nitrate and tannin give precipitates. Fehling's solution and gold chloride are reduced. Potassium cyanide and potassium hydroxide give a blood red color. Like the other aloins it is only precipitated well from a slightly ammoniacal solution, or by ammonio lead acetate.

M.P. 220. C, 57.39%; H, 7.82%; O, 34.79%.

SARSASAPONIN.

Glucoside, yielding sugar and sapogenin (C, 64.61%; H, 10.74%; O, 24.62%). Soluble in alcohol; and in water with foaming, difficultly soluble in chloroform, insoluble in water.

M.P. 228. C, 52.90%; H, 5.20%; O, 41.90%.

APIIN.

Glucoside, yielding sugar and apigeniin, M.P. 210-122. Gives a gelatinous precipitate with silver nitrate, mercuric chloride and copper sulphate. Ferric chloride gives a brownish red and ferrous sulphate a blood red color.

M.P. 228–230. C, 77.41%; H, 2.75%; O, 19.84%.

FRANGULIN.

Glucoside, yielding sugar and emodin, M.P. 254. Deep red (Borntraeger reaction) with KOH or ammonia, red precipitate with barium hydroxide.

M.P.——. C, 53.50%; H, 5.74%; O, 40.76%.

GAULTHERIN.

Glucoside, yielding sugar and methyl salicylate. Easily decomposed by ferments.

M.P. ——. C, 52.08%; H, 5.96%; O, 41.96%.

XANTHORHAMNIN.

Glucoside, yielding by hydrolysis sugar and rhamnetin. KOH solution gives a deep yellow color and ferric chloride a dark brown. Ammonio silver nitrate and Fehling's solution are reduced in the cold. Soluble in alcohol and water, insoluble in ether, chloroform and benzene.

M.P.——. (darkens at 195). C, 52.31%; H, 6.67%; O, 41.02%. . . . . ,. .SENEGIN.

Glucoside, yielding sugar and sapogenin, foams with water. Sulphuric acid gives a yellowish color, changing to reddish yellow and on warming to dark reddish violet, and on dilution with water gives a black precipitate. Sulphuric acid with potassium dichromate gives a deep green contact ring.

M.P. ——. C, 52.31%; H, 6.67%; O, 41.02%.

. SAPOTOXIN.

Glucoside, yielding by hydrolysis sugar and sapogenin. Sulphuric acid gives a yellow to yellowish red color. Solutions foam with water. Easily soluble in alkalies and hot alcohol and in a mixture of alcohol and chloroform but insoluble in ether

M.P. ——. C, 64.39%; H, 4.39%; O, 31.22%.

POLYGALIC ACID (Senega).

Glucoside, yielding sugar and sapogenin. Sulphuric acid gives reddish yellow, red, and finally dark red color, becoming dark violate on warming. Sulphuric acid with potassium dichromate gives a green contact ring. Solutions foam in water. Also precipitated by neutral lead acetate.

M.P. ——. C, 51.0%; H, 7.0%; O, 42.0%. .ERICOLIN.

Hygroscopic bitter needles. Alcohol and alcohol-ether

mixture, difficultly soluble in pure ether, and other common organic solvents.

M.P. ——.   C, 55.46%; H, 7.56%; O, 36.98%.

MENYANTHIN.

Glucoside, yielding sugar and menyanthol.   Precipitated by alkaloidal reagents.

M.P.——.   C, 54.63%; H, 5.47%; O, 39.90%.

LUPININ.

Glucoside, yielding sugar and lupigenin by hydrolysis.

M.P. ——.   C, 55.55%; H, 7.41%; O, 37.04%.

SMILASAPONIN.

Glucoside, yielding sugar and sapogenin (C, 64.61%; N, 10.77%; O, 24.62%).   Solutions foam with water when shaken.

M.P. ——.   C, 37.50%; H, 1.88%; S, 20.00%; Al, 5.63%; O, 34.99% . . . . ALUMNOL.

White powder soluble in water, difficultly soluble in alcohol and insoluble in other common organic solvents.

SOLUBLE IN WATER (ACID), NOT PRECIPITATED BY NEUTRAL OR BASIC LEAD ACETATE

C. PRECIPITATED BY ALKALOIDAL REAGENTS, OR EXTRACTED FROM ALKALINE AQUEOUS LIQUIDS BY IMMISCIBLE SOLVENTS.   NITROGEN PRESENT IN ALL

A. *Extracted by benzene from acid solution*

M.P. 67.   C, 44.25%; H, 4.25%; Cl, 29.90%; N, 7.49%; O, 17.66%.

HYPNAL (Antipyrine chloral-hydrate).

White octahedral crystals.   Colored blood red by ferric chloride.   Yields chloroform on heating with KOH solution. Warmed with ammonio silver nitrate it reduces a silver mirror.   No color with sulphuric acid.

M.P. 102. C, 79.18%; H, 5.60%; N, 9.00%; O, 6.22% . . . . .EXALGINE (Methylacetanilide).

M.P. 128–129. C, 71.58%; H, 6.66%; N, 4.91%; O, 16.85% . . . . .PIPERINE.

Sulphuric acid gives a blood red color decolorized by dilution with water. Nitric acid followed by KOH solution also gives a blood red color. Colorless flat four-sided prisms. With sulphuric acid and formaldehyde a permanent bright green is produced; with sulphuric acid and potassium dichromate a purple, changing to reddish brown and finally a dirty green color. Nitric acid gives an orange red. Sulphuric acid alone gives a yellowish brown changing to greenish brown.

M.P. 140–145. C, 76.03%; H, 8.00%; N, 3.86%; O, 12.11% . . . . .NARCEINE.

M.P. 143–147. C, 66.16%; H, 6.26%; N, 3.50%; O, 24.08% . . . . .COLCHICINE.

Sulphuric acid gives an intense yellow. Sulphuric acid with nitric acid gives a yellow, changing to green, greenish blue, blue, blue violet, and finally to a yellowish wine red. Ferric chloride gives a blackish green on warming. Not precipitated by platinic chloride or picric acid. Gold chloride precipitate is amorphous.

M.P. 145 (also 120). Dry C, 71.60%; H, 5.07%; N, 4.17%; O, 19.16% . . . . .BERBERINE.

Nitric acid precipitates berberine nitrate from concentrated solutions. Potassium or ammonium hydroxide gives a deep red. Chlorine water gives a red colored solution, which on the addition of ammonium hydroxide gives a blackish precipitate. Potassium dichromate gives a crystalline precipitate. Solutions are decolorized by zinc and sulphuric acid, the yellow color being restored by nitric acid. All salts are yellow.

M. 171. C, 74.70%; H, 7.41%; N, 8.64%; O, 9.88%.
                                        QUINIDINE.

(See below).

M.P. 229–234. C, 44.33%; H, 5.15%; N, 33.96%; O, 16.56% . . . . CAFFEINE.

Sublimes at about 80° C. Difficultly soluble in cold water, soluble in alcohol and other organic solvents. A very weak base. Evaporated with hydrochloric acid and a crystal of potassium chlorate and the residue moistened with ammonium hydroxide, a purple color is produced (murexid test). Not precipitated by iodopotassium iodide or potassium mercuric iodide. Precipitated by phosphotungstic acid (sodium salt) potassium bismuthic iodide, etc.

M.P. 255. C, 77.55%; H, 7.48%; N, 9.53%; O, 5.44% . . . . CINCHONINE.

(See below).

M.P. 268. C, 46.66%; H, 4.45%; N, 31.11%; O, 17.78%.

THEOPHYLLINE (Theocine; dimethylxanthine).

White bitter crystals. Soluble in 180 parts of water, diff. sol. in alcohol, insoluble in ether. Forms soluble compounds with alkalies. Murexid test (see caffeine) positive. Precipitated by tannin. If the alkaline (KOH) solution be treated with sulphanilic acid and an excess of hydrochloric acid and a little sodium nitrite added (diazo test), a bright red color is produced (difference from caffeine and theobromine).

M.P. 330. C, 46.66%; H, 4.44%; N, 31.11%; O, 17.79% . . . . THEOBROMINE.

Sublimes at about 170° or 175° C. Murexid test (see caffeine), positive. Not precipitated by potassio-mercuric iodide, potassio-bismuthic iodide, platinic chloride or gold chloride. Precipitated by sodium phosphotungstate (yellow). Best separated from caffeine by its slightly better solubility in benzene or ether.

M.P.——. . . . . AGURINE (Theobromine sodium-acetate).

White crystalline powder, soluble in water and easily splitting into its constituents. Silver nitrate gives a bluish white precipitate, ferric chloride a reddish brown and cupric

sulphate a blue one. Not readily precipitated by iodo-potassium iodide or potassio-mercuric iodide.

B. *Extracted from alkaline solution*

1. EXTRACTED BY PETROLEUM ETHER

Liquid, B.P. −3.5. C, 61.02%; H, 15.25%; N, 23.73%; O, absent . . . . TRIMETHYLAMINE.

Volatile liquid resembling ammonia.

Liquid, B.P. 247. C, 74.08%; H, 8.64%; N, 17.28%; O, absent . . . . NICOTINE.

Rotates polarized light to left but salts are dextrorotatory. Patinic chloride precipitate, M.P. 275, Picrate 218   Volatile, very poisonous

Liquid, B.P. ? C, 75.79%; H, 8.07%; N, 4.91%; O, 11.23% . . . . LOBELINE.

Sulphuric acid gives a yellow color. Hydrochloride melts at 129° C , precipitated by gold and platinic chlorides.

Liquid B.P. 311. C, 76.92%; H, 11.11%; N, 11.97%.
SPARTEINE.

Soluble in chloroform but difficultly soluble in benzene, and petroleum ether, hence most of the alkaloid is apt to be found in the chloroform separate.

Liquid, B P. 166° C. C, 76.81%; H, 12.00%; N, 11.20% . . . . CONIINE.

Sulphuric acid gives a red color changing to green. Right rotary to polarized light. Potassium cadmium iodide gives an amorphous precipitate. The hydrochloride salt melts at 220° C., the platinic chloride double salt at 175, the gold salt at 77 and the picrate at 75.

M.P. 96–98. C, 67.32%; H, 6.93%; N, 4.63%; O, 21.12% . . . . COCAINE.

Strong local anesthetic and mydriatic. Potassium dichromate or chromic acid gives yellow leaflets, potassium permanganate violet precipitate. The mercuric chloride precipi-

tate melts at 122–123. Sulphuric acid gives no color but on warming and then cooling the solution crystals of benzoic acid separate.

2. Extracted by Benzene

Liquid, B.P. 210. C, 68.78%; H, 12.10%; N, 8.92%; O, 10.20% ....Valyl (Valeric acid diethylamide).

Liquid, B.P. 195. C, 68.08%; H, 10.63%; N, 9.93%; O, 11.36%.....................Pelletierine.
Reduces solutions of silver nitrate and gold chloride. Not precipitated by platinic chloride. No color with nitric acid. Sulphuric acid with a trace of selenous acid gives a bluish green changing to dark green and finally to pink.

Liquid, B.P. ? C, 61.92%; H, 8.38%; N, 9.06%; O, 20.64% .... Arecoline.
Chemically quite like pelletierine. Platinum chloride precipitate melts at 176, and is quite soluble. Hydrochloride melts at 157.

Liquid, B.P. ? C, 61.85%; H, 7.21%; N, 14.42%; O, 16.52% .... Pilocarpidine.

M.P. 34. C, 63.46%; H, 7.69%; N, 13.46%; O, 15.39% ....Pilocarpine.
No color with sulphuric acid, with sulphuric acid and potassium dichromate a bright grass green. Triturated with mercuric chloride a black reduction results

Liquid, B.P. 195. C, 68.08%; H, 10.63%; N, 9.93%; O, 11.36% .... Isopelletierine.

Liquid, B.P. 215. C, 69.67%; H, 10.95%; N, 9.03%; O, 10.37% .... Methyl Pelletierine.

M.P. 48. C, 70.58%; H, 9.80%; N, 9.15%; O, 10.47% ....Pseudo Pelletierine.

M.P. 46–48. C, 36.48%; H, 5.41%; N, 9.46%; S, 10.81%; O, 37.84%.

Cheiroline (From wall flower).

M.P. 52–53. C, 67.06%; H, 5.89%; N, 8.23%; O, 18.82% . . . . Tussol (Antipyrine mandelate).

White crystalline powder. Odor of bitter almonds on heating. Heated with KOH solution it yields antipyrine and potassium mandelate.

M.P. 59. C, 66.89%; H, 7.54%; N, 4.59%; O, 20.98% . . . . Hyoscine (Scopolamine).

Gold chloride precipitate melts when crystallized at 198° C. Picric acid precipitate melts at 188° C. Platinic chloride precipitates

M.P. 67–68. C, 71.00%; H, 11.24%; N, 8.28%; O, 9.48% . . . . Lupinine.

Precipitated by gold chloride, platinic chloride and mercuric chloride. The acid sulphate is soluble in absolute alcohol (diff. from associated alkaloids).

M.P. 68. C, 70.86%; H, 7.87%; N, 5.51%; O, 15.76% . . . . Emetine.

Froehde's reagent gives a dirty green color (diff from cephæline, which is purple), changing to grass green with hydrochloric acid

M.P. 72. C, 54.37%; H, 4.85%; N, 4.53%; O, 36.25% . . . . Apolysin.

Soluble in water, alcohol and glycerin.

M.P. 79. C, 74.26%; H, 5.54%; N, 4.56%; O, 15.64% . . . . Cusparidine.

M.P. 91–92. C, 66.25%; H, 5.52%; N, 8.59%; O, 19.64% . . . . Antipyrine Salicylate.

Decomposed by hydrochloric acid into salicylic acid (free) and by sodium or potassium hydroxide into antipyrine (free), for which see tests. Soluble in hot water and alcohol, difficultly soluble in ether. Ferric chloride gives a deep red to violet color, tannin a milky precipitate and strong nitric acid a green color.

M.P. 96–102. C, 77.06%; H, 5.92%; N, 4.36%; O, 14.96% . . . . CEPHÆLINE.

Soluble in all common organic solvents, being more soluble in hot petroleum ether than is emetine. It is also soluble in KOH solution. Froehde's reagent gives a purple color changing to Prussian blue on the addition of hydrochloric acid.

M.P. 99. C, 71.45%; H, 6.79%; N, 8.62%; O, 13.14%.

CHINAPHENIN (Quinine carbonic ester of phenetidin).

Difficultly soluble in water, soluble in most organic solvents. Forms salts with acids and gives the thalleioquin reaction for quinine but gives a yellow herapathite.

M.P. 100. C, 72.98%; H, 7.43%; N, 9.46%; O, 10.13% . . . . EXALGINE.

Soluble in water and most organic solvents. Heated with KOH solution and a little chloroform it gives a faint pleasant odor.

M.P. 100. C, 70.00%; H, 6.64%; N, 7.10%; O, 16.26% . . . . BRUCINE.

Strong nitric acid gives a brick red to scarlet color

M.P. 100.5 (95 hydrated). C, 61.85%; H, 7.22%; N, 14.43%; O, 16.50% . . . . . . PHENOCOLL (Free base).

Exists generally as hydrochloride in a white microcrystalline powder. Soluble in alcohol and water but difficultly soluble in other organic solvents except in the free state.

M.P. 104. C, 68.46%; H, 8.18%; N, 4.20%; O, 19.16%. . . . . ALPHA-EUCAINE.

Exists generally as hydrochloride. Chromic acid solution gives a yellow precipitate (diff. from cocaine). Potassium iodide gives a turbidity and on standing a crystalline precipitate. Mercuric chloride gives a white precipitate, and potassium permanganate a violet one. Warmed with ferric chloride an orange color is produced.

M.P. 105–106.   C, 65.45%; H, 7.64%; N, 15.28%; O, 11.63% . . . . PHYSOSTIGMINE.

Sulphuric acid gives a yellow color.   Nitric acid a yellow changing to olive green.   P sulphate warmed with ammonium hydroxide gives a red changing to reddish yellow, green, greenish blue and (on drying) blue color.   Mayer's reagent gives a precipitate melting at 70.

M.P. 105–106.   C, 57.14%; H, 9.53%; N, 33.33%.
          LYSIDIN (Methyl glyoxalidine).

White hygroscopic needles, easily soluble in water, alcohol, and chloroform, but insoluble in ether.   Gives precipitates with alkaloidal reagents.

M.P. 106–108.   C, 55.03%; H, 12.11%; N, 7.41%; O, 25.45% . . . . DATURINE.

Qualitative tests like those of hyoscyamine and atropine.

M.P. 108.   C, 55.03%; H, 12.11%; N, 7.41%; O, 25.45% . . . . HYOSCYAMINE.

Qualitative tests like atropine except the melting points of the gold chloride precipitate 163° C., the platinic chloride precipitate 206° C., and the picrate 161–3° C.

M.P. 108 (impure).   See *M.P. 115–116* . . . . ATROPINE.

M.P. 108.   C, 67.53%; H, 7.36%; N, 18.18%; O, 6.93%.
   PYRAMIDON (Phenyl-dimethyl dimethylaminopyrazolon).

White alkaline crystals.   Soluble in water, alcohol and most organic solvents.   Ferric chloride gives a blue violet color, nitric acid a blue violet, silver nitrate an intense violet black precipitate of silver and platinic chloride a black one of platinum.   Mercuric chloride gives a crystalline precipitate.

M.P. 111.   C, 73.79%; H, 6.15%; N, 4.53%; O, 15.53% . . . . GALIPEDINE.

M.P. 112–113. C, 70.21%; H, 6.23%; N, 14.89%; O, 8.52% . . . . ANTIPYRINE.

Nitric acid gives with the solutions a green to red color, ferric chloride a deep red and sulphuric acid a yellow.

M.P. 114. C, 77.72%; H, 6.82%; N, 6.36%; O, 9.10%.

QUININE LYGOSINATE (Quinine compound of dioxy-dibenzal-acetone).

Yellow amorphous powder, soluble in common organic solvents and decomposed by acids and alkalies yielding about 71% of quinine.

M.P. 115. C, 74.30%; H, 6.50%; N, 4.33%; O, 14.87% . . . . GALLIPEINE.

M.P. 115–116. C, 55.03%; H, 12.11%; N, 7.41%; O, 25.45% . . . . ATROPINE.
(See also M.P. 108).

Evaporated with nitric acid and the residue treated with alcoholic KOH solution, a violet to red color is produced (see also 108 hyoscyamine). The gold chloride precipitate melts at 135 to 137, the platinic chloride one at 207 to 208. The *alcoholic* solution warmed with mercuric chloride gives a yellow precipitate changing to red. Reacts alkaline directly with phenolphthalein and strongly dilates the pupil of the eye.

M.P. 120 (decomp.). C, 64.54%; H, 8.55%; N, 3.42%; O, 23.49% . . . . DELPHININE.

M.P. 120. C, 70.29%; H, 10.46%; N, 5.88%; O, 13.37% . . . . CARPAINE (from papaw tree).

M.P. 120. C, 74.54%; H, 7.27%; N, 8.49%; O, 9.70% . . . . MENISPERMINE.

M.P. 125 (decomp.) (hydrochloride). Free base C, 72.84%; H, 7.35%; N, 4.47%; O, 15.34%.

DIONIN (Ethylmorphine).

M.P. 128–129.   C, 71.58%; H, 6.66%; N, 4.91%; O,
16.85% . . . . .PIPERINE.
Sulphuric acid gives a blood red color which is decolorized
by dilution with water.   Nitric acid followed by KOH gives
also a blood red color.

M.P. 135.   C, 67.99%; H, 5.38%; N, 3.96%; O,
22.67% . . . . .CHELIDONINE.
Tincture of guaiac followed by sulphuric acid gives a car-
mine red color.

M.P. 130.   See *Trigonelline.*

M.P. 132.   C, 65.79%; H, 5.48%; N, 3.65%; O,
25.08% . . . . .HYDRASTINE.
Sulphuric acid gives a pale yellow color which becomes
reddish purple on warming.   Sulphuric acid and a little
manganese dioxide gives an orange yellow, cherry red, car-
mine, and finally orange yellow color.   With morphine and
sulphuric acid it gives a yellow color changing to purple, and
the above with the addition of potassium dichromate gives a
purple color at once.   Nitric acid gives an orange color.

M.P. 138–146.   C, 73.31%; H, 6.75%; N, 4.50%;
O, 15.44% . . . . .OXYACANTHINE.

M.P. 140–145.   C, 76.03%; H, 8.00%, N, 3.86%;
O, 12.11% . . . . .NARCEINE.
(See also M.P. 170).
Nitric acid gives a fading yellow color, iodine a blue one.

M.P. 147.   C, 70.79%; H, 6.20%; N, 4.13%; O,
18.88% . . . . .PAPAVERINE.
Sulphuric acid on warming gives a deep purple color chang-
ing to violet.

M.P. 155.   C, 72.24%; H, 7.02%; N, 4.64%; O,
16.06% . . . . .CODEINE.
Sulphuric acid gives no color, but with a trace of nitric
acid added it gives a red one.   Ferric chloride (dilute) gives

a blue. Warmed with sulphuric acid a violet color is pro-
duced. With sulphuric acid and a little formaldehyde a
violet color is also produced (diff. from morphine).

M.P. 156. C, 66.10%; H, 8.47%; N, 11.86%; O,
13.57%.

NOVOCAINE (Hydrochloride of paraaminobenzoyl
diethylaminoethanol).

Fine white needles. Free base when precipitated by
alkalies is a congealing oil which slowly crystallizes. M.P.
58–60 (with 2 H_2O, M.P. 51). Soluble in most organic
solvents.

M.P. 158-160. C, 67.00%; H, 9.64%; N, 7.10%; O,
16.30% . . . . GELSEMINE.

No color with sulphuric acid, but with potassium dichro-
mate it gives a reddish brown, reddish and finally green
color. Warmed with nitric acid it gives a reddish color
changing to dark green. The hydrochloride is insoluble in
alcohol, and the nitrate difficultly soluble in water. Gold
and platinic chlorides produce amorphous precipitates.

M.P. 162. C, 78.10%; H, 8.87%; N, 8.28%; O,
4.75% . . . . ASPIDOSPERMATINE.

Perchloric acid gives a deep red color. Sulphuric acid
and also this with potassium dichromate give no color.

M.P. 163. . . . . . . EUMYDRIN (Methylatropine nitrate).

White crystalline salt, soluble in water and alcohol.
Mydriatic.

M.P. 160-163. C, 68.66%; H, 5.72%; N, 3.81%; O,
21.61% . . . . BETA HOMOCHELIDONINE.

M.P. 169 (Hydrochloride). Free base C, 69.06%; H,
9.35%; N, 10.07%; O, 11.52%. Hydrochloride
of benzoyl 2 ethyl 1–3 tetramethyldiamidopropan.

ALYPIN.

White crystalline powder, easily soluble in water. Potas-
sium iodide gives a precipitate, potassium dichromate a yellow

crystalline one, and potassium permanganate a violet one changing to brown on standing. Warmed to 100° C. with ten parts of sulphuric acid and water added, there is given the characteristic odor of the benzoic ethyl ester. Local anesthetic and mydriatic.

M.P. 173 (dry).   C, 74.07%;   H, 7.41%;   N, 8.64%; O, 9.88% .... QUININE.

The aqueous solutions when treated with bromine water and then ammonium hydroxide give a fine emerald green color (thalleioquin test).   If one part of quinine be dissolved in twenty parts of acetic acid, six parts of alcohol and one part of sulphuric acid added, the whole heated to boiling and seven parts of a saturated solution of iodine in alcohol added, slowly, bronze or olive green crystals insoluble in water will slowly separate on cooling.   Solutions with a trace of sulphuric acid when neutralized by ammonia and a drop of hydrogen dioxide and copper sulphate solution added gives on boiling an intense red color which changes to blue and finally to green.

M.P. 171.   C, 74.07%;   H, 7.41%;   N, 8.64%;   O, 9.88% .... QUINIDINE.

Gives the last test given under "quinine."

M.P. 173.   C, 68.29%;   H, 6.23%;   N, 3.79%;   O, 21.69% .... HEROIN (Diacetylmorphine).

Practically insoluble in water and ether, soluble in alcohol, chloroform and benzene.   Forms salts with acids.   Saponified with KOH solution or hydrochloric acid it yields morphine and acetic acid.   Reactions similar to those of morphine but does not liberate iodine from iodic acid, and does not give a blue color at once with potassium ferricyanide and ferric chloride.   Ferric chloride alone gives no color.   Potassium ferrocyanide is reduced.

M.P. 176.   C, 63.92%;   H, 5.57%;   N, 3.39%;   O, 27.12% .... NARCOTINE.

Sulphuric acid gives no color at first but slowly a yellow orange, and finally red color forms.   Nitric acid gives a blood red color.

M.P. 180. C, 64.62%; H, 7.71%; N, 2.04%; O, 25.63% .... VERATRINE.

Sulphuric acid gives a yellow color changing to deep red.

M.P. 180. C, 70.10%; H, 8.60%; N, 4.80%; O, 16.50% .... EUPHTHALMIN.

Occurs generally as the hydrochloric acid salt. Mydriatic. The base is a mandelic acid derivative of Beta-eucaine.

M.P. 182. C, 68.86%; H, 5.72%; N, 3.81%; O, 21.61% .... ALPHA HOMOCHELIDONINE.

M.P. 189 (hydrochloride). *Free base 121.* Free base C, 72.49%; H, 7.40%; N, 9.39%; O, 10.72%.

HOLOCAINE.

Occurs mostly as the hydrochloric acid salt, soluble in water and alcohol. Precipitated by silver nitrate, ammonium hydroxide and general alkaloidal reagents. Local anesthetic.

M.P. 195–197. C, 63.25%; H, 7.28%; N, 2.17%; O, 27.30% .... ACONITINE.

Sulphuric acid gives no color, and none is given by nitric acid. Potassium permanganate gives a blood red precipitate, or with acetic acid frequently red crystals. Characteristic numbing of the tongue produced by weak solutions, physiological test is the most important of all.

M.P. 200–210 (decomp.). C, 76.40%; H, 6.36%; N, 5.25%; O, 11.99%. APOMORPHINE.

Exists as hydrochloride to which the above melting point refers. Sulphuric acid gives no color directly, but with a trace of selenous acid it gives a dark blue color, fading to violet and finally to black. With sulphuric acid and a trace of nitric acid a blood-red color fading to orange, and with sulphuric acid containing ferric chloride a pale blue. Nitric acid alone gives a deep purple color fading to orange. Sulphuric acid and a small crystal of potassium nitrate give a red coloration to the latter, and on stirring the solution becomes green, then blue, then purple and finally cherry red.

M.P. 203–205.   C, 77.55%;   H, 7.48%;   N, 9.53%;
O, 5.44% . . . . CINCHONIDINE.

With potassium sulphocyanide it gives characteristic stellate feathery crystals under the microscope.

M.P. 203.   C, 72.62%;   H, 4.90%;   N, 4.03%;   O,
18.55% . . . . CHELERYTHRINE.

Soluble in alcohol, ether and chloroform, practically insoluble in water.   Reddish salts.

M.P. 205–206.   C, 78.10%;   H, 8.87%;   N, 8.28%;
O, 4.75% . . . . ASPIDOSPERMINE.

Warm perchloric acid gives a deep red color, platinic chloride gives a blue precipitate.   Sulphuric acid with peroxide of lead gives a brown, cherry red and finally purple color.

M.P. 207.   C, 68.36%;   H, 4.84%;   N, 4.00%;   O,
22.80% . . . . PROTOPINE.

Sulphuric acid gives a yellow, red and finally purple color. Sulphuric acid with ferric chloride gives a violet.

M.P. 207.   C, 59.11%;   H, 7.10%;   N, 7.65%;   O,
26.24% . . . . ADRENALINE.

Aqueous solutions yield precipitates with ammonia, KOH solution, etc., and with alkaloidal reagents.   Ferric chloride gives an emerald green, KOH a red color.   Reduces Fehling's solution and ammonio silver nitrate.

M.P. 212.   (Generally impure and variable).

CURARINE.

M.P. 213.   C, 71.85%; H, 4.49%; N, 4.13%; O, 19.53%.
SANGUINARINE.

Red salts with acids but the free base is practically colorless.   Sulphuric acid gives a dark reddish yellow color and nitric acid a brownish yellow.

M.P. 218 (with water of crystallization M.P. 130).

TRIGONELLINE.

Precipitates with bromine in hydrobromic acid, iodopotassium iodide, phosphomolybdic acid, etc.

M.P. 229. Dry C, 44.33%; H, 5.15%; N, 33.96%; O, 16.56% ....CAFFEINE.

 White silky needles. Soluble in water, alcohol, chloroform, benzene, less so in ether. Sublimes readily at 178° C. When evaporated with hydrochloric acid and a little potassium chlorate the residue acquires a deep purple color on exposure to ammonia vapors. Sulphuric and nitric acids give no color.

M.P. 232. C. 71.74%; H, 7.61%; N, 7.61%; O, 13.04% ....YOHIMBINE.

 Soluble in alcohol and chloroform, less soluble in ether and benzene. Sulphuric acid with potassium dichromate gives a bluish violet color. Nitric acid gives no color at first but later a yellowish, and on adding KOH solution an orange color. Warmed with sulphuric acid a slight menthol-like odor is produced. Ammonio silver nitrate is reduced. Gold chloride gives a grayish violet precipitate insoluble in hydrochloric acid. Local anesthetic and supposed aphrodisiac. Other elementary analyses of this have given C, 69.00%; H, 8.00%; N, 7.00%; O, 16.00%. The associated yohimbenine melts at 135, is readily soluble in ether and more nearly corresponds with this last analysis in composition

M.P. 238–240. C, 64.32%; H, 9.43%; N, 258%; O, 23.67% ....SABADINE.

M.P. 238–240. C, 75.91%; H, 9.00%; N, 3.49%; O, 11.69% ....JERVINE.

 Gold and platinic chlorides precipitate. Sulphuric acid gives a color changing from yellow to green.

M.P. 240–246. C, 77.80%; H, 10.72%; N, 3.49%; O, 7.99% ....RUBIJERVINE.

 Gold and platinic chlorides give precipitates. Sulphuric acid gives a play of color changing from yellow to green and finally to red.

M.P. 244. C, 61.23%; H, 9.12%; N, 1.37%; O, 28.28% ....SOLANINE.

 A glucosidal alkaloid which on hydrolysis yields glucose and solanidine, M.P. 191.

M.P. 250. C, 74.76%; H, 5.92%; N, 4.36%; O, 14.96% . . . . .CUSPARINE.

M.P. 255 (sublimes at 220). C, 77.55%; H, 7.48%; N, 9.53%; O, 5.44% . . . . .CINCHONINE.

Sulphate melts at 1985° C. Potassium sulphocyanide gives branching arboraceous feathery micro-crystals

M.P. 263 (decomposes). C, 51.42%; H, 8.58%; N, 40.00% . . . . .HEXAMETHYLENAMINE.

Mercuric chloride gives a precipitate which finally becomes crystalline. Bromine water gives a tetrabromide derivative, which on drying over sulphuric acid passes into the dibromide melting at 198° C. Distilled with sulphuric acid and water it yields formaldehyde and ammonium sulphate. Soluble in chloroform. Warmed with sulphuric acid and a trace of salicylic acid a red color is produced. Precipitated by tannin.

M.P. 265–266. C, 75.44%; H, 6.59%; N, 8.35%; O, 9.62% . . . . .STRYCHNINE.

Sulphuric acid gives no color but when a sharp crystal of potassium dichromate is drawn through the mixture a violet purple streak is produced. Sulphuric acid with ammonium vanadate gives a deep violet blue. Evaporated with nitric acid and treated with ammonia an orange color is produced which on the addition of alcoholic KOH changes to reddish purple and finally to brown.

M.P. 268 (decomp.). C, 72.87%; H, 8.50%; N, 5.66%; O, 12.97% . . . . .BETA EUCAINE (Free base).

Precipitated by alkalies and most alkaloidal reagents but *not* by mercuric chloride (diff. from Alpha Eucaine). Sulphuric and nitric acids give no color reactions. 2 c.c. of a 1% solution with 5% of iodo-potassium iodide solution give a brown color and after about two hours a slight dark brown precipitate, the supernatant fluid remaining clear (diff. from Alpha Eucaine).

M.P. 271. C, 73.47%; H, 7.75%; N, 5.71%; O, 13.07% with HCl . . TROPACOCAINE HYDROCHLORIDE (Benzoylpseudotropine hydrochloride).

Colorless easily soluble needles. The free base is not stable. Boiled with hydrochloric acid it yields benzoic acid and tropine Local anesthetic..

3. SOLUBLE IN CHLOROFORM

M.P. —. C, 43.80%; H, 10.95%; N, 10.22%; O, 35.03% . . . . MUSCARINE.

Practically insoluble in ether. Precipitated by alkaloidal reagents. Strong base forming deliquescent salts.

M.P. —. . . . . CORNUTINE (Keller).

Extracted from neutral or faintly acid solutions. Precipitated by picric acid, iodo-potassium iodide, iodomercuric iodide, and bromine water. Sulphuric acid gives a violet color, which appears slowly Sulphuric acid with a trace of ferric chloride gives an orange yellow color *with a bluish green zone*

4. EXTRACTED BY A MIXTURE OF CHLOROFORM (75) AND ALCOHOL (25)

M.P. 44. C, 55.81%; H, 11.70%; N, 32.49%; PIPERAZINE (dry) (Diethylenediamine).

White hygroscopic crystals. Easily soluble in water. Strongly alkaline and forms easily soluble salts with acids. Potassio-bismuthic iodide gives a characteristic scarlet red precipitate. Nessler's reagent gives a white precipitate, and cupric sulphate a blue one.

M.P. 165-175 (decomp.). C, 43.37%; H, 6.03%; N, 16.86%; O, 33.74%.

HEXAMETHYLENAMINE METHYLENE CITRATE.

White easily soluble powder. Decomposed by acids and alkalies, yielding formaldehyde. Phloroglucin with KOH solution gives a deep rose red.

M.P 255. C, 71.58%; H, 6.67%; N, 4.91%; O, 16.84% . . . . MORPHINE.

Sulphuric acid gives no color when cold but a brown one on warming, or a dark brown color on the addition of a little potassium iodate. Nitric acid produces an orange red color fading to yellow. Sulphuric acid with a trace of molybdic acid, produces a purple color changing to blue, and with a trace of formaldehyde an intense purple color. Ferric chloride gives a green color with neutral solutions.

M.P. 250–255. C, 45.45%; H, 7.58%; N, 10.60%; O, 36.37% . . . . LYCETOL.

Tartrate of a methyl derivative of piperazine. Easily soluble in water. Alkalies liberate the insoluble free base.

M.P. 330 (sublimes 290). C, 46.66%; H, 4.44%; N, 31.11%; O, 17.79%. . . . . THEOBROMINE.

SOLUBLE IN WATER, NOT PRECIPITATED BY LEAD SALTS OR BY ALKALOIDAL REAGENTS

D. FINAL RESIDUE

Extracted by Immiscible Organic Solvents

CRYSTALLINE

M.P. 47–50. C, 40.44%; H, 7.86%; N, 15.73%; O, 35.97% . . . . URETHANE.

Easily soluble in water, alcohol and ether. Warmed with KOH solution an odor of ammonia is produced. Warmed with sulphuric acid, carbon dioxide, alcohol, and ammonium sulphate are formed. Warmed with sodium carbonate, water and iodine, iodoform is produced.

M.P. 58. (Dry.) C, 14.57%; H, 1.82%; Cl, 64.15%; O, 19.46%. . . . . HYDRATED CHLORAL.

Warmed with KOH solution an odor of chloroform is produced. Nessler's solution produces a brick red precipitate, which changes to a dirty yellow and finally green. Boiled with sodium thiosulphate a turbid brick red liquid is

formed which on the addition of KOH solution changes to a clear brownish red.

M.P. 75. C, 60.60%; H, 7.07%; O, 32.33%.

GUAIMAR (Guaiacol glyceryl ester).

White crystalline powder, decomposed by acids and alkalies.

M.P. 75. C, 57.43%; H, 8.31%; O, 34.26%.

PICROCROCIN.

Glucoside, yielding glucose and a terpene on hydrolysis. Colorless bitter prisms.

M.P. 78. (Dry.) C, 24.53%; H, 3.57%; Cl, 53.98%; 17.92% . . . . . CROTON (Butyl) CHLORAL HYDRATE.

M.P. 83-84. C, 49.04%; H, 5.72%; N, 3.87%; S, 8.72%; O, 32.71% . . . . SINALBIN.

Traces of KOH solution color it an intense yellow. Precipitated by mercuric nitrate and silver nitrate. Destroyed by the ferment of the seeds unless extracted by strong alcohol.

M.P. 80-100. C, 55.46%; H, 7.56%; O, 36.98%.

PINIPICRIN.

Yellowish brown, generally amorphous powder. Very bitter Glucoside, yielding sugar and ericinol by hydrolysis.

M.P. 119-120. C, 68.62%; H, 5.00%; O, 26.38%.

XANTHOXYLINE (Southern).

Difficultly soluble in water. Not precipitated from its KOH solution by carbon dioxide. Snow white crystals.

M.P. 120-125. C, 51.95%; H, 6.50%; O, 41.55%.

GENTIOPICRIN.

Glucoside, yielding by hydrolysis sugar and gentiogenin. Sulphuric acid gives no color but on warming gives a carmine red color. Ammonio silver nitrate is reduced directly, but no Fehling's solution.

M.P. 125.   C, 62.17%; H, 8.74%; O, 29.09%.

GRATIOLIN.

Glucoside, insoluble in ether   Sulphuric acid gives a dark red color.   Bitter silky needles.

M.P. 126–127.   C, 28.91%; H, 4.33%; N, 3.37%; S, 15.42%; K, 9.39%; O, 33.68%....SINIGRIN.

By hydrolysis with ferment it yields essential oil of mustard, and must consequently be removed from the seeds by strong alcohol   Barium chloride gives no precipitate in the cold, but on warming precipitates barium sulphate.   Precipitated by silver nitrate and mercuric nitrate.

M.P. 131–132.   C, 69.63%; H, 5.50%; O, 24.88%.

XANTHOXYLINE (Northern).

White needles difficultly soluble in water and cold alcohol. Slightly soluble in ether, readily soluble in chloroform and benzene.   Precipitated from KOH solution by carbon dioxide.

M.P. 134.   C ——? .... LINAMARIN.

Glucoside, yielding sugar and hydrocyanic acid on hydrolysis.   No color with sulphuric acid (diff. from amygdalin).

M.P. 169.   C, 65.45%; H, 5.46%; O, 29.09%.

HYDROCHINOL.

Ferric chloride gives a green color (yellow if iron is in excess).

M.P. 171.   C, 57.99%; H, 5.88%; O, 36.13%.

NARINGIN.

Glucoside, yielding by hydrolysis sugar and naringenin M.P. 248.   Rhombic prisms.   Bitter.   Ferric chloride and ammonium hydroxide give each a brownish red color.   Soluble in hot water and alcohol but difficultly soluble in other common organic solvent.

M.P. 171.   C, 40.00%; H, 6.67%; O, 53.33%.

TRIOXYMETHYLENE.

Paraformaldehyde.   Soluble in water, insoluble in most organic solvents.   Heated, it liberates formaldehyde.

M.P. 175–176. C, 54.54%; H, 6.29%; O, 39.17%.

METHYL ARBUTIN.

Glucoside, yielding sugar and methylhydroquinone. Soluble in water and alcohol, slightly in ether.

M.P. 179. C, 60.78%; H, 7.84%; O, 31.38%.

STROPHANTHIN (S. Kombe).

Crystals, insoluble in ether and benzene. Sulphuric acid gives a green, orange, red, and on warming, brown, and again green. Sulphuric acid followed by a little water and furfural gives a red violet color with a characteristic spectrum. Glucoside, yielding sugar and amorphous Strophanthidin.

M.P. 180. C, 56.34%; H, 6.10%; O, 37.56%.

POPULIN.

Glucoside, yielding by hydrolysis sugar, benzoic acid and Saligenin M.P. 82. Sulphuric acid gives a red color. Heated with sulphuric acid and potassium dichromate it yields salicylic aldehyde (odor). Insoluble in ether.

M.P. 183–184. Free base C, 65.81%; H, 8.02%; N, 5.91%; O, 20.26%.

GUAJASANOL (Diethylglycocollguaiacol hydrochloride).

Colorless prismatic crystals. Decomposed by saponifying with potash solution. Soluble in water, alcohol and ether.

M.P. 185. C, 56.14%; H, 6.43%; O, 37.43%.

CONIFERIN.

Slightly bitter needles. Sulphuric acid gives a dark violet to red color. Dried with phenol and hydrochloric acid gives a deep blue. Insoluble in ether.

M.P. 188. C, 52.94%; H, 5.88%; O, 41.18%.

ARBUTIN.

Glucoside, yielding sugar and hydrochinone. Ferric chloride gives a blue color. Soluble in water, alcohol, and slightly in ether.

M.P. 192. C, 54.83%; H, 6.45%; O, 38.72%.

SYRINGIN.

Tasteless needles, insoluble in ether. Glucoside, yielding sugar and syringetin, M.P. 208. Sulphuric acid gives a dark blue.

M.P. 200 (dry 125–130). C, 52.51%; H, 5.91%; N, 3.06%; O, 38.52%. . . . . AMYGDALIN.

Glucoside, yielding sugar, hydrocyanic acid and benzoic aldehyde.

M.P. 203–204. C, 71.42%; H, 9.53%; O, 19.05%.

OXAPHOR (Oxycamphor).

White crystalline powder, soluble in water and all organic solvents. Depressant to respiratory center but not to the circulation.

M.P. 204. C, 67.09%; H, 7.35%; O, 25.56%.

ALPHA QUASSIN (Picrasmin).

Bitter crystals, easily soluble in chloroform.

M.P. 209–212. C, 67.50%; H, 7.50%; O, 25.00%.

BETA QUASSIN (Surinam).

Bitter crystals soluble in chloroform.

M.P. 208 (softens). C, 76.36%; H, 9.99%; O, 13.65%; or C, 68.10%; H, 8.59%; O, 23.31%. . . BRYONIN.

Glucoside, yielding sugar and bryogenin, M.P 210 (softens at 130). Bitter refractive leaflets. Insoluble in ether and chloroform.

M.P. 210. C, 54.54%; H, 6.29%; O, 39.17%.

SALICIN.

Glucoside, yielding sugar and saligenin, M.P. 82. Sulphuric acid gives an intense red color. Rhombic brilliant bitter needles.

M.P. 217. C, 65.21%; H, 8.69%; O, 26.10%.

DIGITALIN.

Masses of needles. Soluble in alcohol and chloroform but difficultly in ether. Sulphuric acid gives a yellow color, with

the addition of bromine water a rose red to violet one. Keller's test (see below) gives a fiery red zone. Glucoside, yielding by hydrolysis sugar and digitaligenin. M.P 210–212 Solutions in water foam on shaking. If the acetic acid solution be floated in a test tube over sulphuric acid containing a trace of ferrous sulphate, a red zone forms at the point of contact while the upper layer slowly becomes yellowish brown and the lower one golden yellow, red, and finally red violet.

M.P. 218. C, 50.55%; H, 5.38%; O, 44.07%.

SCOPOLIN.

Glucoside, yielding by hydrolysis sugar and scopoletin (Methylæsculetin).

M.P. 220. C, 45.90%; H, 2.73%; N, 7.65%. S, 12.02%; O, 31.70% . . . . SACCHARIN.

· White, disagreeably sweet, crystalline powder, slightly soluble in water but readily soluble in alkalies. Difficultly soluble in ether and chloroform. Sulphuric acid gives no color.

M.P. 229. C, 63.81%; H, 8.75%; O, 27.44%.

ANDROMETOXIN.

Soluble in water, alcohol and chloroform, difficultly soluble in ether. Hydrochloric acid gives a red color.

M.P. 230–232. C, ... DIGITALEIN CRYSTALLINE.

Gives Keller's reaction like digitoxin, i.e., if the acetic acid (glacial) solution of the glucoside with a trace of ferric chloride be floated over sulphuric acid, a fiery red zone is formed at the point of contact while the upper acetic acid solution becomes yellow to brown and the sulphuric acid golden yellow, red, and finally violet.

M.P. 235. C, 53.21%; H, 7.60%; O, 39.19%.

DIGITONIN.

Watery solutions of the glucoside foam strongly on shaking. Heated with hydrochloric acid for a long time a granite red color is produced. Sulphuric acid with a trace of ferrous sulphate gives a yellow color. Keller's test (see above) gives

a weak rose colored zone.   If a one to one thousand solution in hydrochloric acid S.G 1.19 be heated in a boiling water bath for five minutes a yellow color is formed which changes to dark yellow and finally to a beautiful red; by strongly cooling now a clear blue and finally again a red is produced. By hydrolysis it gives sugar and digitogenin, M.P. 250.

M.P. 240 (dry) (145 air dry).   C, 63.95%; H, 8.44%; O, 27.61% . . . . Digitoxin.

With sulphuric acid and a trace of ferrous sulphate it gives a dirty brownish red.   With Keller's test (see above) it gives a dirty brown green zone at the point of contact while the upper glacial acetic acid solution becomes an intense blue green and the lower sulphuric acid becomes brown or perhaps red after a day or more.   By hydrolysis it yields sugar and digitoxigenin, M.P. 225.

M.P. 250.   C, 75.78%; H, 7.37%; G, 16.85%.

Helleborin.

Colorless needles, insoluble in cold water   Sulphuric acid gives a deep violet color. Hydrolysis yields sugar and helleborein.

M.P. 265.   C, 78.43%; H, 11.11%; O, 10.46%.

Urson.

Tasteless silky needles from Uva ursi.

M.P. ?   C, 62.10%, H, 3.88%; O, 34.02%.

Colocynthin (resinous).

Soluble in alcohol but difficultly soluble in ether and chloroform   Glucoside.

M.P. ?   C, 36.37%; H, 6.06%; N, 21.21%; O, 36.37%.

Asparagin.

Insoluble in chloroform.

M.P. ?   C, 63.17%; H, 9.60%, O, 27.23%.

Convallarin.

Glucoside.   Right-angled crystals.   Insoluble in ether.

M.P. ?   C, 53.91%; H, 8.59%; O, 37.50%.

Convallamarin.

Glucoside.   Bitter crystalline powder.

M.P. C, ... Apocynein.

 Glucoside resembling in its action digitalin and strophanthin.

M.P. ? C, 53.55%; H, 7.72%; O, ... Scillain.

 Glucoside, yielding sugar, butyric acid, and isopropyl alcohol.

M.P. ? C, 57.64%; H, 7.42%; O, 34.94%.

Dulcamarin.

 Glucoside.

M.P. C, 50.47%; H, 6.69%; O, 42.84%. . . . Crocin.

 Glucoside, yielding sugar and crocetin. Soluble in alcohol, slightly in ether. Sulphuric acid gives a deep blue color.

Amorphous

Glycerin (ol).

 Thick liquid. Heated with a borax bead in a non-luminous flame the characteristic greenish color and spectrum of boric acid is produced. Sweetish taste.

Miscellaneous

8.5% of silver combined with albumen. . . . Protargol.
Tannate of casein . . . . Protan.
Silver caseinate, soluble . . . . Argonin.
20–25% of silver combined with vitellin. . . . . . Argyrol.
10% silver nitrate and ethylenediamine . . Argentamine.

TABLE II

ELEMENTARY ANALYSES OF ORGANIC MEDICINAL CHEMICALS ARRANGED IN THE ORDER OF THEIR CARBON CONTENT

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
3.04	0.25	—	—	—	96.67	Iodoform
5.82	1.45	15.15	—	—	Br 77.18	Bromal hydrate
8.40	0.19	—	2.45	—	88.96	Iodol
8.51	1.43	—	—	—	I 90.06	Ethylene iodide
9.07	0.38	8.09	—	—	Br 30.26 Bi 52.20	Xeroform
10.06	0.84	—	—	—	89.10	Chloroform
12.76	2.14	—	—	—	Br 85.10	Ethylene bromide
14.57	1.82	19.46	—	—	64.15	Hydrated chloral
14.74	0.40	—	—	—	Br 94.86	Bromoform
15.39	3.23	—	—	—	I 81.38	Ethyl iodide
15.43	2.25	5.15	—	—	77.17	Brometone
15.86	2.22	63.42	18.50	—	—	Nitroglycerin
15.89	1.99	63.58	18.54	—	—	Tetranitrol
17.38	1.03	3.33	—	—	78.26	Losophan
18.75	1.56	25.00	—	—	Cl 54.69	Dichloracetic acid
18.78	2.08	16.73	7.30	—	55.11	Chloralamide
20.33	1.35	8.15	—	—	Bi 70.17	Betanaphthol bismuth
21.75	0.91	4.84	—	—	72.50	Tribromphenol
22.01	4.62	—	—	—	Br 73.37	Ethyl bromide
22.13	3.08	9.85	—	—	64.94	Isopral
24.26	4.07	—	—	—	Cl 71.67	Ethylene chloride

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
24.53	3.57	17.92	—	—	53.98	Butyl chloral
26.07	4.38	69.55	—	—	—	Formic acid
26.66	2.23	71.11	—	—	—	Oxalic acid
27.12	3.99	—	—	—	59.79	Chloretone
27.27	—	—	—	72.73	—	Carbon disul.
28.91	4.33	38.68	3.37	15.42	K 9.39	Sinigrin
30.25	2.94	20.18	5.88	—	As 31.09 Na9.66	Atoxyl
31.44	1.31	48.91	18.34	—	—	Picric acid
31.58	5.26	63.16	—	—	—	Glycollic acid
31.81	5.04	42.42	3.72	16.99	—	Myronic acid
32.00	4.00	64.00	—	—	—	Tartaric acid
32.30	5.10	14.20	—	—	35.90	Bromural
33.02	2.61	35.99	—	—	Bi 28.48	Bismal
33.46	2.42	45.57	—	—	Na 18.55	Citarine
34.28	4.7	60.95	—	I 41 64	—	Alphozone
35.40	1.64	6.20	4.59	Cl	—	Vioform
35.82	4.48	59.70	—	11.53	—	Malic acid
36.36	6.06	36.37	21.21	—	—	Asparagin
36.37	1.53	8.22	—	—	Cl 53.88	Trichlorphenol
36.48	5.41	37.84	9.46	10.81	—	Cheiroline
36.84	7.01	28.08	—	28.07	—	Sulfonal
37.22	7.81	—	—	—	Cl 54.97	Ethyl chloride
37.46	12.58	49.96	—	—	—	Methyl alcohol
37.50	4.17	58.33	—	—	—	Citric acid
37.50	12.50	50.00	—	—	Al	Methyl alcohol
37.50	1.88	34.99	—	20.00	5.65	Alumnol
38.61	16.21	—	45.18	—	—	Methylamine
38.71	16.13	—	45.17	—	—	Methylamine
39.13	8.70	52.17	—	—	—	Glycerin

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
39.34	7.69	52.75	—	—	—	Dulcite, mannite
39.67	7.43	26.44	—	26 44	—	Trional
39.91	13.40	—	46.69	—	—	Ethylenediamine
40.00	3.33	56.65	—	—	—	Curacao aloin
40.00	6.67	53.33	—	—	—	Acetic acid, lactic acid, glucoses, paraform
40.44	7.86	35.97	15.73	—	—	Urethane
40.68	5.09	54.23	—	—	—	Succinic acid
41.09	4.10	8.83	—	—	45.95	Thymol iodide
41.38	3.45	55.17	—	—	—	Maleic acid, aconitic acid, fumaric acid
41.38	6.90	—	24.13	27.59	—	Thiosinamine
42.00	2.00	56.00	—	—	—	Meconic acid
42.10	6.43	51.47	—	—	—	Saccharoses, arabic acid, triticin
43.29	4.12	52.59	—	—	—	Citarine
43.37	6.03	33.74	16.86	—	—	Hexamethylenamine, urethane citrate
43.75	6.30	50.19	—	—	—	Quinic acid
43.80	10.95	35.03	10.22	—	—	Muscarine
43.90	7.20	48.90	—	—	—	Quercite
44.21	5.26	50.53	—	—	—	Behenic acid
44.25	4.25	17.66	7.94	—	29.90	Hypnal
44.33	5.15	16.56	33.96	—	—	Caffeine
44.44	9.63	35.55	10.37	—	—	Betaine
44 44	3.70	—	51.85	—	—	Hydrocyanic acid
44.44	6.17	49.39	—	—	—	Cellulose, dextrin
44.44	4.76	51.80	— ·	—	—	Starch, cyclopin
45.65	2.17	52.24	—	—	—	Chelidonic acid
45.90	2.73	31.70	7.65	12.02	—	Saccharin
46.66	4.45	17.78	31.11	—	—	Theobromine, theophylline
47.87	5.85	34.05	3.72	8.51	—	Sinalbin

TABLE II—*Continued*

Carbon. %	Hydro-gen. %	Oxygen. %	Nitro-gen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
47.88	6.68	39.89	5.55	—	—	Linamarin
48.65	8.11	43.24	—	—	—	Propionic acid
49.04	5.72	32.71	3.81	8.72	—	Sinalbin
49.41	3.63	47.06	—	—	—	Gallic acid (dry)
49.48	5.15	16.51	28.86	—	—	Caffeine
49.48	12.39	26.44	11.57	—	—	Cholin
49.60	4.92	43.26	2.22	—	—	Indican (?)
50.24	6.81	24.13	18.37	—	—	Conglutin
50.42	10.92	26.89	11.77	—	—	Muscarine
50.47	6.69	42.84	—	—	—	Crocin
50.55	5.38	44.07	—	—	—	Scopoline
51.00	6.70	25.40	16.10	0.80	—	Gluten, Casein (?)
51.00	7.00	42.00	—	—	—	Ericolin
51.02	4.89	44.87	—	—	—	Fraxin
51.20	9.46	27.38	11.96	—	—	Amyl nitrite
51.24	7.16	23.28	16.38	1.04	P 0.94 Ag 20– 25%	Argyrol
51.42	8.58	—	40.00	—	—	Hexamethylen- amine
51.47	7.02	24.29	16.82	0.40	—	Legumin
51.95	6.49	6.93	—	—	54.63	Monobromated camphor
31.95	6.50	41.55	—	—	—	Gentiopicrin
52.01	5.88	42.11	—	—	—	Cinchona tannin
52.07	4.96	42.97	—	—	—	Aesculin
52.08	5.96	41.96	—	—	—	Xanthorhamnin
52.17	3.10	43.73	—	—	—	Nutgall tannin
52.29	7.24	21.06	18.09	1.32	—	Vitellin
52.31	6.67	41.02	—	—	—	Senegin, sapotoxin
52.39	4.78	42.83	—	—	—	Daphnin
52.40	3.67	43.93	—	—	—	Pyrogallol tannins
52.44	6.42	41.14	—	—	—	Verbenalin
52.45	6.81	22.21	15.65	0.80	—	Albumin
52.47	5.79	40.23	1.53	—	—	Laurocerasin
52.51	5.91	38.52	3.06	—	—	Amygdalin
52.53	7.38	40.27	—	—	—	Helleborin

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
52.60	7.00	21.49	18.06	0.85	—	Gliadin
52.86	4.84	42.30	—	—	—	Thujin
52.90	5.20	41.90	—	—	—	Apiin
52.94	5.88	41.18	—	—	—	Arbutin
52.94	4.71	42.35	—	—	—	Aesculin
53.00	7.00	22.00	15.70	0.80	P 0.8	Casein
53.04	6.36	—	—	—	—	Aurantiamarin
53.04	3.05	43.91	—	—	—	Tannoform
53.20	3.45	43.35	—	—	—	Tannigen
53.21	7.60	39.19	—	—	—	Digitonin
53.22	15.64	—	31.14	—	—	Ethylamine
50-54	6.5-7.5	?	15-17	1.5-2.0	P 0.4-0.8	Albumens
53.33	5.19	41.48	—	—	—	Cinchona red
53.48	6.16	—	—	—	—	Aurantiamarin
53.50	5.74	40.76	—	—	—	Gaultherin
53 70	6.10	40.20	—	—	—	Arbutin
53.80	7.30	38.90	—	—	—	Scillain
53.85	5.13	41.02	—	—	—	Oak tannin
53.88	3.80	37.26	5.06	—	—	Tannopin
53.91	8.59	37.50	—	—	—	Convallamarin
54.08	4.72	41.20	—	—	—	Datiscin
54.11	6.90	21.48	16.63	0.88	—	Mucedin
54.50	9.15	36.35	—	—	—	Ethyl acetate
54.52	9.15	36.33	—	—	—	Amylene hydrate
54.52	9.15	36.33	—	—	—	Paraldehyde
54.54	7.18	38.28	—	—	—	Quillajic acid
54.54	3.90	41.56	—	—	—	Protocatechuic acid
54.54	6.29	39.17	—	—	—	Methylarbutin
54.54	6.29	39.17	—	—	—	Salicin
54.55	9.09	36.36	—	—	—	Butyric acid
54.63	5.47	39.90	—	—	—	Lupinin
54.64	5.04	40.32	—	—	—	Ruberythric acid
54.77	5.39	39.84	—	—	—	Hesperidin
54.81	6.73	38.46	—	—	—	Syringin

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
54.87	7.37	37.50	—	—	—	Convolvulin
54.91	5.50	39.56	—	—	—	Hesperidin, barosmin
54.96	9.93	24.42	10.69	—	—	Hedonal
54.96	9.92	24.43	10.69	—	—	Leucin
55.03	12.11	25.45	7.41	—	—	Atropine, hyoscyamine
55.08	5.57	39.35	—	—	—	Rubian
55.10	8.16	36.74	—	—	—	Convolvulin
55.29	7.83	36.87	—	—	—	Cyclamin
55.38	7.70	39.92	—	—	—	Scillain
55.40	7.60	36.90	—	—	—	Saponin (?)
55.43	6.53	21.74	7.61	8.69	—	Sinapin
55.46	7.56	36.98	—	—	—	Menyanthin
55.46	7.56	36.98	—	—	—	Pinipicrin
55.55	7.41	37.04	—	—	—	Smilasaponin
55.60	5.60	38.80	—	—	—	Naringin
55.63	1.99	42.38	—	—	—	Ellagic acid
55.81	11.70	—	32.49	—	—	Piperazine
55.81	6.99	37.20	—	—	—	Crotonic acid
55.90	4.35	39.75	—	—	—	Quercitrin
56.03	3.92	12.47	—	—	Cl 27.58	Monochlorphenol
56.14	6.43	37.43	—	—	—	Coniferin
56.15	5.81	38.05	—	—	—	Phloridzin
56.34	6.10	37.56	—	—	—	Populin
56.37	6.04	37.59	—	—	—	Ipecac tannin
56.66	7.77	35.57	—	—	—	Jalapin, turpethin
56.75	5.41	37.84	—	—	—	Coffee tannin
56.75	5.40	37 85	—	—	—	Carthamin
56.99	3.60	39.41	—	—	—	Novaspirin
57.13	4.76	38.11	—	—	—	Lenigallol
57.13	4.76	38.11	—	—	—	Phloroglucin, pyrogallol
57.14	9.53	33.33	—	—	—	Lysidin
57.15	4.76	38.09	—	—	—	Orsellic acid

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine Bromine, Iodine	
57.32	7.01	35.67	—	—	—	Globularin
57.39	7.82	34.79	—	—	—	Sarsasaponin
57.43	8.31	34.26	—	—	—	Picrocrocin
57.49	5.40	28.72	8.39	—	—	Orthoform (new)
57.53	4.11	38.36	—	—	—	Thujagenin
57.64	7.42	34.94	—	—	—	Dulcamarin
57.69	13.46	15.38	13.46	—	—	Amanitin (?)
57.73	3.78	38.49	—	—	—	Cinchona red
57.99	5.88	36.13	—	—	—	Naringin
58.00	5.06	36.87	—	—	—	Scoparin
58.22	5.50	36.28	—	—	—	Curacao aloin
58.82	9.80	31.37	—	—	—	Valeric acid
59.01	7.10	26.24	7.65	—	—	Adrenaline
59.01	7.10	26.24	7.65	—	—	Eumydrin
59.12	7.05	32.27	1.56	—	—	Glycyrrhizin
59.21	3.91	36.84	—	—	—	Quercetin
59.26	6.17	34.57	—	—	—	Capaloin
59.29	5.49	35.22	—	—	—	Mesotan
59.40	4.95	35.65	—	—	—	Rhatany tannin
59.44	5.88	34.68	—	—	—	Nataloin
59.42	5.54	34.99	—	—	—	Socaloin
59.47 (0.58)	6.38	34.04	—	17.00	—	Ichthyol (free)
59.63	5.59	34.78	—	—	—	Nataloin
59.63	6.28	31.09	3.02	—	—	Narceine
59.65	4.65	35.70	—	—	—	Catechol tannins
59.66	6.07	26.54	7.73	—	—	Tyrosin
59.78	7.47	32.75	—	—	—	Colocynthin
59.80	5.64	34.56	—	—	—	Ononin
59.92	7.05	32.66	—	—	—	Glycyrrhizic acid
59.95	8.05	32.00	—	—	—	Digitalin
60.00	8.00	32.00	—	—	—	Angelic acid
60.00	4.45	35.55	—	—	—	Aspirin
60.00	8.33	31.67	—	—	—	Bryonin
60.00	4.45	33.55	—	—	—	Acetozone
60.00	4.44	35.56	—	—	—	Cetraric acid

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
60.00	8.00	32.00	—	, —	—	Camphoric acid
60.00	13.33	26.67	—	—	—	Propyl alcohol
60.20	7.69	32.11	—	—	—	Ouabain
60.40	9.00	30.60	—	—	—	Parillin
60.43	8.37	31.20	—	—	—	Parillin
60.46	5.42	34.12	—	—	—	Aspidium tannin
60.50	5.88	33.62	—	—	—	Picrotoxin
60.53	6.82	28.50	4.15	—	—	Colchicine
60.57	7.26	27.76	4.42	—	—	Oxyacanthine
60.60	7.07	32.33	—	—	—	Guaiacol glyeryles-ter (guaimar.)
60.66	8.78	28.88	1.68	—	—	Solanine
60.71	5.95	33.34	—	—	—	Barbaloin
60.78	7.84	31.38	—	—	—	Strophanthin
60.87	4.34	34.79	—	—	—	Salicylic acid
60.90	4.81	34.23	—	—	—	Catechin
61.01	11.86	27.13	—	—	—	Acetal.
62.02	15.25	—	23.73	—	—	Trimethylamine
61.03	8.56	25.27	5.14	—	—	Jervine
61.22	6.13	32.65	—	—	—	Fortoin
61.23	9.12	28.28	1.37	—	—	Solanine
61.29	8.85	26.40	3.46	—	—	Sabadilline
61.34	3.49	33.17	—	—	—	Podophyllotoxin
61.39	6.67	29.77	2.17	—	—	Aconitine
61.53	11.11	27.36	—	—	—	Hedonal
61.69	8.78	26.76	2.77	—	—	Sabadine
61.85	5.15	33.00	—	—	—	Meconine
61.85	7.22	16.50	14.43	—	—	Phenocoll
61.85	7.21	16.52	14.42	—	—	Pilocarpidine
61.86	5.15	32.99	—	—	—	Benzohelicin
61.90	10.40	27.70	—	—	—	Acetone
61.92	8.38	20.64	9.06	—	—	Arecoline
62.07	10.35	27.58	—	—	—	Capronic acid
62.07	3.45	34.48	—	—	—	Lenteolin
62.10	3.88	34.02	—	—	—	Colocynthin (resinous)

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
62.15	6.78	22.10	8.97	—	—	Thermodin
62.17	8.81	29.02	—	—	—	Gratiolin
62.17	4.81	33.02	—	—	—	Rhatany, red (Phlobaphene)
62.33	6.49	31.17	—	—	—	Crocin
62.50	4.17	33.33	—	—	—	Anemonin
62.68	7.46	29.88	—	—	—	Antiarin
62.68	6.26	31.06	—·	—	—	Filicic acid
62.92	4.72	32.36	—	—	—	Linin
63.13	5.26	31.58	—	—	—	Vanillin
63.15	5.33	31.52	—	—	—	Vanillin
63.15	11.57	25.28	—	—	—	Terpin hydrate
63.15	5.26	31.59	—	—	—	Resorcinol monacetate (Euresol)
63.15	7.18	19.98	6.69	—	—	Lactophenin
63.16	9.60	27.24	—	—	—	Convallarin
63.25	7.28	27.30	2.17	—	—	Aconitine
63.44	6.58	25.20	—	—	—	Colchiceine
63.46	7.69	15.39	13.46	—	—	Pilocarpine
63.53	3.54	32.93	—	—	—	Purgatin
63.57	4.63	31.79	—	—	—	Hemotoxylin
63.60	8.50	27.90	—	—	—	Digitoxin
63.64	6.06	30.30	—	—	—	Physalin, Filicic acid
63.80	8.20	24.90	3.10	—	—	Veratroidine
63.81	8.75	27.44	—	—	—	Andrometoxin
63.92	5.57	27.12	3.39	—	—	Narcotine
63.95	8.44	27.61	—	—	—	Digitoxin
64.12	11.44	24.44	—	—	—	Oenanthic acid
64.20	6.17	29.63	—	—	—	Filicin
64.32	9.43	23.67	2.58	—	—	Sabadine
64.39	4.39	31.22	—	—	—	Polygalic acid
64.42	8.70	23.97	2.91	—	—	Veratrine
64.51	6.46	29.05	—	—	—	Monotal
64.51	6.45	29.04	—	—	—	Cantharidin
64.54	8.55	23.49	3.42	—	—	Delphinine

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
64.55	8.66	23.47	3.42	—	—	Delphinine
64.62	7.71	25.63	2.04	—	—	Veratrine (true)
64.79	13.60	21.61	—	—	—	Ethyl ether
64.80	13.51	21.62	—	—	—	Butyl alcohol
64.86	6.48	28.66	—	—	—	Apiol
64.97	8.29	24.38	2.36	—	—	Cevadine
65.11	3.87	31.02	—	—	—	Gentisin
65.21	8.69	26.10	—	—	—	Digitalin
65.26	6.66	28.07	—	—	—	Cussin
65.30	8.96	25.74	—	—	—	Chinovin
65.45	7.64	11.63	15.28	—	—	Physostigmine
						Resorcinol
65.45	5.46	29.09	—	—	—	Pyrocatechol, Hydrochinol
65.45	6.66	19.41	8.48	—	—	Euphorin
65.45	6.66	19.41	8.48	—	—	Anæsthesin
65.49	7.64	11.60	15.27	—	—	Physostigmine
65.62	3.13	31.25	—	—	—	Purpurin
65.62	4.76	29.62	—	—	—	Purpurin
65.64	15.15	—	18.21	—	—	Diethylamine
65.69	5.11	29.20	—	—	—	Guaiacol carbonate
65.69	5.11	29.20	—	—	—	Santalin
65.79	5.48	25.08	3.65	—	—	Hydrastine
65.81	8.02	20.26	5.91	—	—	Guajasanol
66.10	8.47	13.57	11.86	—	—	Novocaine
66.08	6.08	16.26	8.11	—	—	Chlorophyl (pure)
66.08	6.66	23.20	4.06	—	—	Eupyrine
66.16	6.26	24.08	3.50	—	—	Colchicine
66.25	5.52	19.63	8.60	—	—	Antipyrine salicylate
66.44	6.57	22.15	4.84	—	—	Cocaine
66.59	3.82	29.59	—	—	—	Emodin
66.66	3.71	29.63	—	—	—	Umbelliferon
66.67	6.67	26.66	—	—	—	Quassin
66.67	3.70	30.63	—	—	—	Emodin
66.89	7.54	20.98	4.59	—	—	Hyoscine (scopolamine)

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
67.00	9.64	16.30	7.10	—	—	Gelsemine
67.04	7.25	17.80	7.82	—	—·	Phenacetin
67.06	5.89	18.82	8.23	—	—	Tussol (antipyrine mandelate)
67.09	7.35	25.56	—	—	—	Quassin (picrasmin)
67.11	5.43	27.46	—	—	—	Brazilin
67.31	8.31	21.68	2.70	—	—	Pseudojervine
67.32	6.93	21.12	4.63	—	—	Cocaine
67.41	5.62	26.96	—	—	—	Cubebin
67.41	5.62	26.96	—	—	—	Curcumin
67.50	7.50	25.00	—	—	—	Quassin (Surinam)
67.50	8.40	20.50	3.60	—	—	Staphisagrine
67.53	7.36	6.93	18.18	—	—	Pyramidon
67.60	4.20	28.20	—	—	—	Frangulic acid
67.71	5.88	26.41	—	—	—	Picropodophyllin
67.74	6.45	—	25.81	—	—	Guaiacol
67.76	6.45	25.81	—	—	—	Orcine
67.99	5.38	22.67	3.96	—	—	Chelidonine
68.04	8.24	16.51	7.21	—	—	Triphenin
68.06	5.08	14.32	12.34	—	—	Chelidonine
68.08	10.63	11.36	9.93	—	—	Pelleterine
68.10	8.59	23.31	—	—	—	Bryonin
68.18	7.58	24.24	—	—	—	Absinthin
68.18	13.63	18.19	—	—	—	Amylic alcohol
68.25	5.70	26.05	—	—	—	Curcumin
68.29	6.23	21.69	3.79	—	—	Heroin
68.36	4.84	22.80	4.00	—	—	Protopine
68.46	8.18	19.16	4.20	—	—	α Eucaine
68.57	5.30	26.13	—	—	—	Salophen
68.62	5.00	26.38	—	—	—	Xanthoxylin (S.)
68.66	5.72	21.61	3.81	—	—	Homochelidonine
68.78	12.10	10.20	8.92	—	—	Valyl
68.85	4.92	26.23	—	—	—	Benzoic acid
68.85	4.92	26.23	—	—	—	Guaiacol-salol
68.86	8.10	23.04	—	—	—	Elaterin

Table II—*Continued*

Carbon. %	Hydro- gen. %	Oxygen. %	Nitro- gen. %	Sulphur. %	Metals, Phos- phorus, Chlo- rine, Bro- mine, Iodine.	
68.96	8.04	23.00	—	—	—	Elaterin
69.00	8.00	16.00	7.00	—	—	Yohimbine
69.06	9.35	11.52	10.07	—	—	Alypin
69.42	10.74	19.84	—	—	—	Coryfin
69.46	5.27	25.27	—	—	—	Rottlerin
69.63	5.50	24.88	—	—	—	Xanthoxylin (N.)
69.69	7.07	16.17	7.07	—	—	Euquinine
69.76	11.62	18.61	—	—	—	Capric acid
69.84	4.76	25.39	—	—	—	Cotoin
70.00	6.64	16.26	7.10	—	—	Brucine
70.00	9.29	20.71	—	—	—	Capsaicin
70.00	3.33	26.67	—	—	—	Alizarin
70.00	7.50	15.50	7.00	—	—	Yohimbenine (in-active)
70.10	8.60	16.50	4.80	—	—	Euphthalmine
70.11	5.18	24.71	—	—	—	Salicylic aldehyde
70.13	9.09	20.78	—	—	—	Capsicin
70.21	6.23	8.52	14.89	—	—	Antipyrine
70.29	10.46	13.37	5.88	—	—	Carpaine
70.38	8.50	21.12	—	—	—	Absinthin
70.58	7.95	16.60	4.84	—	—	Atropine, hyoscy-amine, etc.
70.59	5.26	19.82	4.33	—	—	Sanguinarine
70.59	5.88	23.53	—	—	—	Furfural, anisic aldehyde, etc.
70.79	6.20	18.88	4.13	—	—	Papaverine
70.86	7.87	15.76	5.51	—	—	Emetine
70.87	3.94	25.19	—	—	—	Chrysophanic acid
70.90	9.50	15.60	3.90	—	—	Delphinoidine
71.00	10.05	18.95	—	—	—	Rottlerin
71.11	6.66	11.86	10.37	—	—	Acetanilide
71.42	9.52	19.06	—	—	—	Diosphenol
71.42	9.53	19.05	—	—	—	Oxaphor (oxy-camphor)
71.43	9.52	19.05	—	—	—	Angelic acid
71.45	6.79	13.14	8.62	—	—	Chinaphenin

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
71.58	6.67	16.84	4.91	—	—	Morphine
71.58	6.67	16.84	4.91	—	—	Piperine
71.59	11.37	9.05	7.99	—	—	Lupinine
71.64	5.08	19.10	4.18	—	—	Berberine
71.64	7.46	—	20.90	—	—	Pyrrol
71.74	7.61	13.04	7.61	—	—	Yohimbine
71.85	4.49	19.53	4.13	—	—	Sanguinarine
72.24	7.02	16.06	4.68	—	—	Codeine
72.31	5.22	22.47	—	—	—	Chrysarobin
72.41	13.79	13.79	—	—	—	Heptyl alcohol
72.48	11.41	16.11	—	—	—	Ricinoleic acid
72.49	7.40	10.72	9.39	—	—	Holocaine
72.62	4.90	18.55	4.03	—	—	Chelerythrine
72.84	7.35	15.34	4.47	—	—	Dionin
72.87	8.50	12.97	5.66	—	—	β eucaine
72.89	4.67	22.44	—	—	—	Salol
72.92	5.41	21.62	—	—	—	Cinnamic acid
72.98	7.43	10.13	9.46	—	—	Exalgine
72.99	5.41	21.60	—	—	—	Cinnamic acid
72.99	6.83	11.87	8.31	—	—	Aristochin
73.17	7.32	19.32	—	—	—	Santonin
73.17	7.32	19.32	—	—	—	Eugeneol
73.28	3.82	12.22	10.68	—	—	Indigo blue (indigotin)
73.31	6.75	15.44	4.50	—	—	Oxyacanthine
73.31	6.75	15.44	4.50	—	—	Berberine
73.46	4.76	21.78	—	—	—	Epicarin
73.47	7.75	13.07	5.71	—	—	Tropacocaine
73.68	12.28	14.04	—	—	—	Myristic acid
73.79	6.15	15.53	4.53	—	—	Gallipedine
73.84	13.84	12.32	—	—	—	Capryllic alcohol
73.85	8.31	4.92	12.92	—	—	Cytisin
73.97	4.11	21.92	—	—	—	Coumarin
74.07	7.41	9.88	8.64	—	—	Quinine
74.07	6.17	19.76	—	—	—	Safrol
74.08	8.62	—	17.28	—	—	Nicotine

TABLE II—*Continued*

Carbon. %	Hydro-gen. %	Oxygen. %	Nitro-gen. %	Sulphur. %	Metals, Phos-phorus, Chlo-rine, Bro-mine, Iodine.	
74.26	5.54	15.64	4.56	—	—	Cusparidine
74.30	6.50	14.87	4.33	—	—	Gallipeine
74.45	8.03	17.52	—	—	—	Salit
74.54	10.56	14.90	—	—	—	Asclepiadin
74.54	7.27	9.70	8.49	—	—	Menispermine
74.57	8.48	9.04	7.81	—	—	Aspidospermine
74.76	5.92	14.96	4.36	—	—	Cusparine
75.00	3.57	21.44	—	—	—	Alizarin
75.00	8.33	16.67	—	—	—	Helenin
75.00	12.50	12.50	—	—	—	Palmitic acid
75.00	11.70	13.30	—	—	—	Validol
75.02	6.66	10.43	8.64	—	—	Quinine and quini-dine
75.04	9.07	15.89	—	—	—	Anacardic acid
75.44	6.59	9.62	8.35	—	—	Strychnine
75.47	4.41	20.12	—	—	—	Phenolphthalein
75.78	7.37	16.85	—	—	—	Helleborine
75.79	8.07	11.23	4.91	—	—	Lobeline
75.91	9.00	11.69	3.40	—	—	Jervine
76.03	8.00	12.11	3.86	—	—	Narceine
76.06	12.68	11.26	—	—	—	Stearic acid
76.36	9.99	13.65	—	—	—	Bryonin
76.40	6.36	11.99	5.25	—	—	Apomorphine
76.52	6.43	17.05	—	—	—	Ethyl alcohol
76.59	12.06	11.35	—	—	—	Oleic acid
75.78	7.37	16.85	—	—	—	Helleborin
76.81	12.00	—	11.20	—	—	Coniine
76.83	8.53	14.64	—	—	—	Helenin
76.84	12.90	10.26	—	—	—	Citronellol, men-thol
76.92	12.82	10.26	—	—	—	Menthol
76.92	11.11	—	11.97	—	—	Sparteine
77.06	5.92	14.96	4.36	—	—	Cephaeline
77.27	4.54	18.19	—	—	—	Betol
77.41	2.75	19.84	—	—	—	Frangulin
77.42	7.53	—	15.05	—	—	Aniline

TABLE II—*Continued*

Carbon. %	Hydrogen. %	Oxygen. %	Nitrogen. %	Sulphur. %	Metals, Phosphorus, Chlorine, Bromine, Iodine.	
77.55	7.48	5.44	9.53	—	—	Cinchonine and cinchonidine
77.69	12.23	—	10.07	—	—	Methylconiine
77.72	6.82	9.10	6.36	—	—	Quinine lygosinate
77.80	10.72	7.99	3.49	—	—	Rubijervine
77.92	11.70	10.38	—	—	—	Cineol, citronellal
77.92	11.69	10.39	—	—	—	Borneol
78.05	10.57	—	11.38	—	—	Sparteine
78.10	8.87	4.75	8.28	—	—	Aspidospermine and aspidospermatine
78.43	11.11	10.46	—	—	—	Urson
78.57	9.52	11.91	—	—	—	Abietic acid
78.68	13.95	7.37	—	—	—	Cetyl alcohol
78.94	10.53	10.53	—	—	—	Camphor
78.94	10.53	10.53	—	—	—	Citral, carvon, thujon, camphor, etc.
78.94	6.33	—	14.73	—	—	Pyridine
78.94	10.53	10.53	—	—	—	Caryophyllin
79.18	5.60	6.22	9.00	—	—	Exalgine
79.24	5.65	15.11	—	—	—	Benzaldehyde
80.00	9.33	70.67	—	—	—	Thymol and carvol
80.70	3.85	15.38	—	—	—	Anthraquinone
81.00	11.70	7.21	—	—	—	Santalol, cubeb, camphor, sesquiterpene camphors
81.08	8.11	10.81	—	—	—	Anethol, eugenol
81.51	13.21	—	5.28	—	—	Curarine
81.55	7.17	6.00	5.28	—	—	Beerbamine
81.55	10.68	7.77	—	—	—	Lactucerin
81.81	14.14	4.05	—	—	—	Cerotyl alcohol
81.82	6.06	12.12	—	—	—	Cinnamic aldehyde Styracin
81.82	11.04	7.14	—	—	—	Lactucerin
82.57	11.36	6.06	—	—	—	Betulin
83.22	16.78	—	—	—	—	Pentane

TABLE II—*Continued*

Carbon. %	Hydro-gen. %	Oxygen. %	Nitro-gen. %	Sulphur. %	Metals. Phosphorus, Chlorine, Bromine, Iodine.	
83.33	5.55	11.12	—	—	—	Betanaphthol
83.72	5.43	—	10.58	—	—	Quinoline
83.87	11.83	4.30	—	—	—	Phytosterin
84.11	15.89	—	—	—	—	Octane
84.11	12.15	3.74	—	—	—	Cholesterin
85.71	14.29	—	—	—	—	Pental
88.15	11.85	—	—	—	—	Pinene, terebene, camphene, fenchene, limonene, dipentene, sylvestrine, terpinine, phellandrene, etc.
88.15	11.65	—	—	—	—	Terpene, pinene, etc.
90.50	9.50	—	—	—	—	Xylene
91.24	8.76	—	—	—	—	Toluene
92.24	7.76	—	—	—	—	Styrol
92.31	7.69	—	—	—	—	Benzene
92.54	7.46	—	—	—	—	Sesquiterpenes, cadinine, cedrine, cubebine, caryophyllene, humulene, etc.
93.75	6.25	—	—	—	—	Naphthalene
94.38	5.62	—	—	—	—	Anthracene

TABLE III

MELTING-POINTS OF SOME COMMONLY-OCCURRING MEDICINAL CHEMICALS AND THEIR DERIVATIVES, ARRANGED IN THE ORDER OF THEIR MAGNITUDE

	Deg. C.		Deg. C.
Oleic acid	−4	Hydrated chloral	58
Benzene	5 5	Capsicin	59
Castor oil fat acids	13	Benzosol	59–61
Hypnone	14	Erythrol tetranitrate	61
Anethol	22	Beeswax	62–63
Sunflower oil fat acids	23	Hypnal	67
Cocoanut fat acids	24 5	Coumarin	67
Olive oil fat acids	26–28	Euquinine	67–68
Guaiacol	28 5	Emetine	68
Cacao butter fat acids	30–33	Trichlorphenol	68
Apiol	30–32	Absinthin	68
Peanut oil fat acids	33	Eserine mercury iodide	70
Sesame oil fat acids	35	Hedonal	74–76
Butter fat acids	38	Thiosinamine	74
Cottonseed oil fat acids	38	Guaiamar	75
Monochlorphenol	40	Trional	76
Wool fat acids	41	Monobromated camphor	76
Oleomargarine fat acids	42	Croton chloral	78
Nutmeg butter fat acids	42 5	Hyoscyamine hydrobromide	78
Menthol	42–43	Cusparidine	79
Phenol	43	Pinipicrin	80
Piperazine (see also 104)	44	Naphthalene	80
Angelic acid	45	Vanillin	80–81
Formalid	46	Chloretone	82
Cheirolin	46–48	Diosphenol	83
Isopral	49	Sinalbin	83–84
Thymol	50–51	Carnauba wax	83–85
Japan wax	50–51	Thermodin	86–88
Urethane	50–51	Guiacol carbonate	86–90
Euphorin	50–51	Eupyrine	87–88
Tussol	52–53	Tetronal	89
Bromal hydrate	53	Anæsthesin	90–91
Stearic acid	56	Antipyrine salicylate	91–92
Quinine×H₂O	57	Betol	95
		Tribromphenol	95

TABLE III—*Continued*

	Deg. C.		Deg. C.
Alphanaphthol......	95	Triphenin..........	120
Euquinine..........	95	Carpaine..........	121
Phenocoll..........	95–100	Holocaine	121
Cephæline..........	92–102	Losophan.........	121 5
Cocaine............	96–98	Picric acid.........	122
Pimpinelline........	97	Betanaphthol.......	122
Oxalic acid × 2H₂O ..	98	Cocaine mercury chlor.	122–125
Kryofine...........	98	Podophyllotoxin	124
Piperine plat. chlor..	100	Gratiolin...........	125
Exalgine...........	100–120	Amygdalin........	125–130
Hematoxylin.	100–120	Dionin (decomp.) ...	125
Colalin.............	103–107	Ethylmorphine......	125
Codeine × 2H₂O	100	Filicic acid (cryst.)..	125
Pinipicrin..........	100	Sulfonal............	125–126
Santalin...........	104	Sinigrin............	126–127
Pyrocatechol.......	104	Triphenylamine.....	127
Piperazine..........	104–107	Cubebin............	128
α Eucaine	104	Piperine...........	128–130
Physostigmine......	105–106	Trigonelline × H₂O ..	130
Lysidine...........	105–106	Pilocarpine	130
Orcinol............	107	Cotoin.............	130
Phloridzine........	108–109	Styracol............	130
Antithermine.......	108	Jalapin.............	131
Pyramidon.........	108	Pyrogallol.....	131
Atropine...........	108	Hydrastine.........	132–135
Hyoscyamine.......	108 5	Tartaric acid.......	135
Resorcinol..........	110	Linamarin..........	135
Helenin	110	Aspirin.............	135
Antipyrine..........	112–113	Corydaline.	135
Acetanilide.........	113	Aconitine g o l d	
Iodine.............	114	chloride.........	135–145
Quinine lygosinate ..	114	Citric acid.........	135–150
Chloralamid........	115	Atropine gold chlorid	135–137
Brucine × H₂O	115	Sparteine sulphate..	136
Sulphur............	115	Oxyacanthine.... ..	138–146
Iodoform...........	115	Colchicine × H₂O	139–140
Alphozone..........	115–127	Salophenin	139
Quinone............	116	Iodol (decomp.).....	140–150
Terpin hydrate......	116–117	Aconitic acid	140
Lactophenin........	117–118	Agaricin............	140
Xanthoxylin........	119–120	Maleic acid.........	140
Gentiopicrin........	120–125	Hyoscyamine sul-	
Delphinine..........	120	phate............	140–160

TABLE III—*Continued*

	Deg. C.		Deg. C.
Orthoform (new). ..	141–143	Vioform............	170–178
Cussin	142	Rosagenin..........	171
Colchicine (dry)	143–150	Naringin...........	171
Digitoxin (air dry) ..	145	Paraformaldehyde...	171
Berberine..........	145	Quinidine..........	171
Bromural...........	146	Heroin.............	173
Curacao or Barbaloin	147	Quinine............	74–175
Papaverine.........	147	Veratrine...........	175
Mescaline..........	150–160	Camphor...........	175
Convolvulin........	150–155	Coniine platinic chlo-	
Aconitine gold		ride...............	175
chloride.........	150–151	Purgatin..........	175–178
Brucine (dry).......	151	Glycophylline.......	175–180
Anemonin..........	152	Castanea quercitrin .	175
Novocaine..........	156	Methylarbutin......	175–176
Salicylic acid........	156–157	Catechin b.........	175–177
β Homochelidonine..	159–160	Parillin.	176
Pilocarpine picrate..	159–160	Narcotine..........	176
Tannigen...........	160	Arecoline platinic	
Inulin.............	160	chloride..........	176
Gelsemine..........	160	Brucine............	176
Iodol picrate........	161–163	Strophanthin.......	178–180
Aspidospermatine...	162	Cusparidine platinic	
Quinic acid.........	162	chloride..........	179
Colchicine..........	162–172	Vicin..............	180
Hyoscyamine gold		Populin............	180
chloride..........	162	Euphthalmine.......	180
Eumydrin..........	163	Veratrine...........	180
Saliformin..........	165–175	Cephælanthin.......	180
Curcumin...........	165–169	Citrophenin.........	181
Antisepsine.........	165–166	Cusparidine platinic	
Hexamethylenamine		chloride..........	182
methylene citrate..	165–175	α Homochelidonine..	182
Sophorin...........	166	Verbenalin..........	182
Brometone.........	167	Villosin.............	183–185
Cusparine gold chlo-		Guajasanol.........	183–184
ride..............	167	Chloralose..........	184–186
Sidonal.............	168	Lactocerin..........	184
Spirosal.............	169–170	Strophanthin..	185
Alypin.............	169	Ouabain...........	185
Arbutin............	170	Anisic acid.........	185
Narceine...........	170	Myrticolorin........	185
Saloquinine	170–190	Coniferin...........	185

TABLE III—*Continued*

	Deg. C.		Deg. C.
Pilocarpidine plat. chloride..........	186–190	Quassin (J.)	204
Chrysophanic acid ..	186–188	Wistarin...:........	204
Hyoscine picrate....	187–188	Japaconitine........	204
Camphoric acid	186–187	Aesculin.............	205
Salophen.............	187–188	Aspidospermine.....	205–210
Hyoscine sulphate...	187	Hyoscyamine platinic chloride.......	206
Arbutin.............	188	Atropine platinic chloride..........	207–208
Holocaine..........	189		
Aristochin..........	189	Protopine..........	207
Datiscin.............	190	Tropacocaine gold chloride..........	208
Epicarin............	190–195		
Rottlerin...........	190–200	Arecaine platinic chloride..........	208
Quinine hydrochloride.........	190	Analagen...........	208
Cusparine gold chloride.............	190	Iridin..............	208
		Bryonin....;......	208
Cerberin............	190–191	Quassin (S.J.).......	209
Veronal............	191	Nataloin............	210
Syringin............	192	Pseudaconitine......	210–212
Cocaine hydrochloride..............	193	Curarine...........	212
Robinin............	195	Cytisine gold chloride	212–213
Aconitine...........	197–198	Arecaine platinic chloride..........	213–214
Hyoscine gold chloride..............	198–199	Nicotine picrate.....	218
		Coniine hydrochloride	220
Salicin.............	199–201	Pseudo-hyoscyamine picrate..........	220
Amygdalin.........	200		
Isatin..............	200	Ecgonine gold chloride..............	226
Daphnine...........	200		
Morphine hydrochloride..............	200	Cordyaline platinic chloride..........	227
Elaterin............	200	Andrometoxin......	229
Trigonelline×H₂O ..	200–218	Yohimbine........	231
Pilocarpine hydrochloride..........	200	Pseud-aconitine gold chloride..........	236–238
Cinchonidine........	202~203	Emodin............	254
Polygonin..........	202–203	Cinchonine (sublimes 220°)............	255
Oxaphor............	203–204		
Chelerythrine.......	203		

TABLE IV

BOILING POINTS

	Deg. C.		Deg. C.
Methyl chloride.....	—24	M. xylene..........	139
Methyl nitrite.......	—12	Allyl sulphide.......	140
Methylamine........	— 6	Isobutylacetate.....	140
Trimethylamine.....	3 5	Ortho xylene........	142
Methyl bromide.....	4 5	Bromoform.........	148
Dimethylamine	7 2	Oenanthylic aldehyde	155
Ethyl chloride......	12	Terebene...........	155–156
Ethyl nitrite........	12–16	Butyric acid........	163
Ethylamine........	18	Coniine............	166
Ethyl aldehyde.	20 8	Myristic aldehyde...	168
Ethyl mercaptan . ..	36	Valeric acid.........	175
Ethyl ether........	36	Isoamyl butyrate....	178
Ethyl bromide......	38	Phenol.............	183(175)
Pentane............	38	Benzaldehyde.......	179
Pental (iso amylene).	36–38	Crotonic acid.......	180
Methyl iodide.......	43	Aniline.............	184 5
Carbon disulphide...	46–47	Angelica acid.......	185
Acetone............	56 5	Valeric acid.........	186
Propylamine........	32–49	Amyl valerate.......	188–190
Chloroform.........	60–61	Ortho cresol	188
Methyl nitrate......	66	Dichloracetic acid...	190
Methyl alcohol......	66 5	Pelletierine.........	195
Ethyl iodide........	72	Salicylic aldehyde...	196
Ethyl acetate.......	72–77	Ethyl glycol........	197 5
Butylamine.........	68–76	Tiglic acid..........	198
Ethyl acetate.......	72–77	Para cresol	198
Ethyl alcohol.......	78 3	Beechwood creosote.	200–220
Benzene............	80 4	Meta cresol.........	201
Isopropyl alcohol. ..	82 7	Guaiacol...........	200–205
Tertiary butylalco- hol..............	83	Valyl..............	210
Amyl nitrite........	96–99	Thymol............	230
Amylene hydrate. ..	99–103	Quinoline...........	237
Acetal	104–106	Pyrocatechol........	245
Toluene............	110	Anisic aldehyde.....	248
Pyridine............	116	Benzoic acid........	250
Ethyl butyrate......	121	Resorcinol..........	276
Paraldehyde........	123–125	Euresol.............	283
P. xylene...........	138	Sparteine...........	311
Acetic anhydride....	137	Cannabinol.........	265 at 20 mm.

TABLE V

TABLE SHOWING THE PERCENTAGE BY VOLUME OF ABSOLUTE ALCOHOL CONTAINED IN AQUEOUS SOLUTIONS OF VARIOUS SPECIFIC GRAVITIES DETERMINED AT 15.6° C.

%		%		%	
1	0.9985	35	0.9591	69	0.8924
2	0 9970	36	0 9577	70	0 8900
3	0 9956	37	0 9563	71	0 8875
4	0 9942	38	0 9549	72	0 8849
5	0 9928	39	0 9534	73	0 8823
6	0 9915	40	0 9519	74	0 8797
7	0 9902	41	0 9503	75	0 8770
8	0 9890	42	0 9487	76	0 8744
9	0 9878	43	0 9470	77	0 8717
10	0 9866	44	0 9453	78	0 8690
11	0 9855	45	0 9436	79	0 8663
12	0 9844	46	0 9419	80	0 8636
13	0 9833	47	0 9401	81	0 8608
14	0 9822	48	0 9382	82	0 8580
15	0 9811	49	0 9363	83	0 8551
16	0 9801	50	0 9344	84	0 8522
17	0 9791	51	0 9324	85	0 8493
18	0 9781	52	0 9304	86	0 8463
19	0 9771	53	0 9284	87	0 8432
20	0 9761	54	0 9264	88	0 8400
21	0 9751	55	0 9243	89	0 8368
22	0 9741	56	0 9222	90	0 8336
23	0 9730	57	0 9200	91	0 8303
24	0 9720	58	0 9178	92	0 8269
25	0 9710	59	0 9156	93	0 8233
26	0 9699	60	0 9134	94	0 8196
27	0 9688	61	0 9111	95	0 8157
28	0 9677	62	0 9089	96	0 8118
29	0 9666	63	0 9066	97	0 8076
30	0 9654	64	0 9043	98	0 8034
31	0 9642	65	0 9020	99	0 7987
32	0 9630	66	0 8996	100	0 7935
33	0 9617	67	0 8973		
34	0 9604	68	0 8949		

TABLE VI

TABLE OF CONSTANTS FOR FATS AND OILS

Fat.	Specific Gravity at 15° C.	Refractive Index.	Melting-point of Acids. Deg. C.	Saponi-fication Number.†	Iodine Number.‡	In-soluble Fat Acids.§
Almond.......	0.915	1.4728	14	190	96	96 2
	0 920	—	—	195	99	—
Beeswax......	0 960	1 4448	60*	91	8	—
	0 970	1 4463	62*	96	11	—
Butter........	0 927	1 4590	38	221	26	87 5
	0 936	1 4620	—	227	35	—
Cacao butter..	0 950	1 4500	52	192	32	94 6
	0 952	—	—	193	37	—
Cod-liver.	0 922	1 4850	21	185	139	95 3
	0 930	—	25	187	152	—
Castor........	0 950	1 480	13	178	83	—
	0 965	—	—	183	86	—
Cocoanut.....	0 897	1 5030	25	250	8	88 6
	0 926	—	—	255	9	—
Cottonseed....	0 922	1 4737	38	190	104	96 2
	0 930	1 4757	—	195	108	—
Croton........	0 940	1 4803	—	210	102	89
	0 955	—	—	215	104	—
Carnauba wax.	0 990	1 4520	84 5*	80	13	—
	0 999	1 4541	—	84	14	—
Chinese wax..	0 970	—	80 5*	63	—	—
Hempseed....	0 925	—	18	190	148	—
	0 930	—	19	193	—	—
Japan wax....	0 970	1 4500	51	220	4	—
	0 980	—	55*	223	7	—
Lard..	0 930	1 4694	35	195	57	96
	0 940	—	—	197	63	—
Linseed.......	0 930	1 4835	17	190	170	95 5
	0 935	—	24	195	180	—
Maize........	0 920	1 4768	18	188	117	96
	0 925	—	21	190	122	—

* M.P. of fat or wax itself.
† Milligrammes of KOH per gramme of fat.
‡ Milligrammes of iodine per gramme of fat.
§ Percentage of insoluble fatty acids.

Tᴀʙʟᴇ VI—*Continued*

Fat.	Specific Gravity at 15° C.	Refractive Index.	Melting-Point of Acids. Deg. C.	Saponification Number.†	Iodine Number.‡	Insoluble Fat Acids.§
Mustard (black)	0.915	1.4672	16	174	106	95
	0 920	—	—	175	—	—
Myrtle wax.......	0 995	—	40	205	10	—
	—	—	44*	210	11	—
Neatsfoot.........	0 910	1 4740	17	189	165	—
	0 920	—	26	197	175	—
Olive.............	0 914	1 4703	26	190	82	95 4
	0 917	1 4718	28	195	85	—
Oleomargarine	0 924	—	42	—	55	95 5
	0 930	—	—	—	—	—
Paraffin...........	varies	1 4340	none	none	2	none
Poppy............	0 920	1 4773	20	193	134	95 4
	0 947	—	—	197	140	—
Peanut...........	0 915	1 4707	26	—	—	95 8
	0 920	1 4731	33	190	95	95 8
	—	—	—	197	98	—
Palm.............	0 920	1 4520	48	195	51	95 6
	0 945	—	—	200	53	—
Rape.............	0 914	1 4520	20	175	99	95 0
	0 917	—	—	178	105	—
Spermaceti........	0 960	—	44–50*	128	8	—
	—	—	—	—	9	—
Sperm............	0 875	1 4664	13	130	84	—
	0 885	1 4683	21	145	—	—
Sunflower.........	0 924	1 4762	23	193	120	95 0
	0 926	—	—	195	130	—
Sesame...........	0 919	1 4748	35	187	105	95 8
	0 924	1 4762	—	191	109	—
Tallow..........…	0 940	1 4420	45	195	36	95 6
	0 952	1 469‖	—	198	40	—
Wool fat..........	0 973	1 4650	41 8	98	25	—
	~	—	—	102	28	—

* M.P. of fat or wax itself.
† Milligrammes of KOH per gramme of fat.
‡ Milligrammes of iodine per gramme of fat.
§ Percentage of insoluble fatty acids.
‖ Oil.

TABLE VII

VOLATILE OILS, ODOR CHARACTERISTIC FOR EACH

1. HEAVIER THAN WATER

A. *Optical Rotation Right* (+)

Specific Gravity.	A/d.	
1.007 to 1.018	+2 to 3°	Jasmine
1 043 to 1 056	4°	Cinnamon, cassia
1 065 to 1 065	4°	Sassafras

B. *Optical Rotation Left* (−)

1 033 to 1 048	−1°	Pimenta (allspice)
1 040 to 1 060	−1°	Cloves
1 045 to 1 055	−1°	Cinnamon, cassia
1 170 to 1 180	0 25 to 1°	Gaultheria, true

C. *Optically Inactive*

1 170 to 1 180	0°	Birch, methyl salicylate
1 045 to 1 060	0°	Bitter almond
1 013 to 1 020	0° B.P. 148–153°	Mustard

2. LIGHTER THAN WATER

A. *Optical Rotation Right* (+)

Specific Gravity.	A/d.	
0.84 to 0.85	+96 to 98°	Orange
0 85 to 0 86	60 to 65°	Lemon
0 86 to 0 87	to 155°	Turpentine
0 84 to 0 86	50°	Erigeron
0 85 to 0 92	16 to 23°	Angelica
0 85 to 0 88	0 6°	Hops
0 85 to 0 88	to 155	Turpentine from Pinus palustris, P. cubensis, etc.
0 86 to 0 92	14 to 28°	Nutmeg
0 86 to 0 87	8 to 13°	Coriander
0 86 to 0 88	0 to 2°(seldom)	Juniper
0 88 to 0 89	18 to 20°	Bergamot
0 88 to 0 90	60°	Leaves of Virginia cedar
0 89 to 0 93	10 to 20°	Mace
0 89 to 0 91	15°	Rosemary
0 90 to 0 92	40 to 60°	Savine
0 90 to 0 92	1 to 15°	Eucalyptus
0 90 to 0 91	70 to 80°	Caraway
0 90 to 0 91	1 to 3°	Anthemis
0 90 to 0 92	70 to 80°	Dill
0 91 to 0 92	10 to 25°	Sage
0 92 to 0 93	18 to 22°	Pennyroyal
0 93 to 0 95	30 to 0.45°	Tansy
0 96 to 0 97	10 to 30°	Calamus
0 96 to 0 97	12 to 24°	Fennel
0 97 to 0 98	1° M.P. 15–19°C.	Anise

TABLE VII—*Continued*

B   *Optical Rotation Left* (−)

Specific Gravity.	A/d.	
0.85 to 0.87	− 4°	Rose
0 86 to 0 87	− 5 to − 10°	Pine
0 86 to 0 88	−11 (seldom+)	Juniper
0 86 to 0 92	− 3 to − 25°	Cedar leaves
0 85 to 0 88	to −155°	Numerous volatile oils from Pinus species, including turpentines, P. Glabra, −31 (except those from P. palustris and P. cubensis, +9 to 12)
0.88 to 0.92	− 3 to − 20°	Citronella
0 88 to 0 89	− 10°	Lavender
0 89 to 0 90	− 7 to − 35°	Copaiba
0 89 to 0 91	−25 to − 35°	Peppermint
0 90 to 0 92	−20 to − 40°	Cubeb
0 90 to 0 93	− 2 to − 3°	Thyme
0 91 to 0 93	−35 to − 45°	Spearmint
0 91 to 0 92	− 2°	Cajuput
0 91 to 0 92	− 3 to − 20°	Cardamon
0 87 to 0 91	− 35°	Origanum
0 89 to 0 90	− 6 to − 10°	Geranium
0 93 to 0 96	− 8 to − 15°	Valerian
0 94 to 0 96	−30 to − 40°	Virginia cedar wood
0 96 to 0 98	− 0 to − 2°	Bay laurel
0 96 to 0 98	− 5°	Wormseed
0 96 to 0 97	−15 to − 20°	Sandalwood
0 96 to 0 98	− 2°	Myrcia

TABLE VIII

PERCENTAGE OF GLYCERIN IN AQUEOUS SOLUTIONS
AT 15° C.—(AFTER SKALWEIT)

Per-centage.	Specific Gravity.	Refractive Index.	Per-centage.	Specific Gravity.	Refractive Index.
2	1.0048	1.3354	52	1.1346	1.4024
4	1 0096	1 3378	54	1 1402	1 4024
6	1 0144	1 3402	56	1 1458	1 4084
8	1 0192	1 3426	58	1 1514	1 4104
10	1 0240	1 3452	60	1.1570	1 4144
12	1 0290	1 3477	62	1 1628	1 4175
14	1 0340	1 3503	64	1 1686	1 4205
16	1 0390	1 3529	66	1 1743	1 4235
18	1 0440	1 3555	68	1 1799	1 4265
20	1 0490	1 3581	70	1 1855	1 4295
22	1 0542	1 3607	72	1 1909	1 4324
24	1 0594	1 3633	74	1 1963	1 4354
26	1 0646	1 3660	76	1 2017	1 4384
28	1 0698	1 3687	78	1 2071	1 4414
30	1 0750	1 3715	80	1 2125	1 4444
32	1 0804	1 3743	82	1 2179	1 4475
34	1 0858	1 3771	84	1 2233	1 4505
36	1 0912	1 3799	86	1 2287	1 4535
38	1 0966	1 3827	88	1 2341	1 4565
40	1 1020	1 3854	90	1 2395	1 4595
42	1 1074	1 3882	92	1 2447	1 4625
44	1 1128	1 3910	94	1 2499	1 4655
46	1 1182	1 3938	96	1 2550	1 4684
48	1 1236	1 3966	98	1 2600	1 4712
50	1 1290	1 3966	100	1 2650	1 4742

TABLE IX
RESINS, GUM RESINS, AND BALSAMS

	Acid Number.	Ester Number.	Saponi- fication Number.	Important Constituents.
Ammoniac...	100–115	30–60	140–180	½ to 2% vol. oil; sp.gr., 0.89; 65–75% resin.
Benzoin......	90–140	70–170	160–265	10–20% of free benzoic and cinnamic acids, 75% resin (benzoresinol and benzoresinotannol esters of cinnamic acid), vanillin.
Canada balsam	80–93	5–9	90–96	20% vol. oil, 80% resin.
Copaiba......	80–88	5–9	90–96	30–60% vol. oil, 40–70% resin (copaivic acid).
Copal.........	60–140	40–80	130–190	10–20% vol. oil, 80–90% resin (kaurolic acids).
Dammar......	50–52	80–85	130–135	10% vol. oil, 90% resin (dammar and dammarolic acids and resins).
Galbanum....	20–60	80–100	140–180	10–20% vol. oil, 80–90% resin (umbelliferon and umb. resinotannol).
Guaiac.......	70–90	—	—	Guaiaretic acid, guaiacic and guaiaconic acids.
Jalap.........	12–14	120–180	130–190	Convolvulin.
Mastic........	50–55	20–22	70–80	1–2% vol. ol, mastichic acid, masticin.
Myrrh........	20–25	125–200	145–225	2–5% vol. oil, 25–50% resin.
Peru balsam..	30–60	160–230	220–250	Benzyl benzoate, 60%, benzyl cinnamate 2%, benz. and cinnam. esters of peruresinotannol, free benz. and cinn. acid.
Rosin........	155–175	92–95	180–190	Abietic anhydride 90%

TABLE IX—*Continued*

	Acid Number.	Ester Number.	Saponi- fication Number.	Important Constituents.
Sandarac.. ..	165–170	75–80	240–250	5% vol. oil, 95% resin (sandaracolic acid and callitrolic acid.)
Scammony ...	10–15	160–170	180–185	Scammonia.
Shellac.......	60–65	150–155	210–215	90% resin, gum.
Tolu balsam ..	120–160	30–40	150–190	7% benzyl benzoate and benzyl cinna- mate, 20% free cinn. acid, 75–80% of resin toluresinotannol cin- namic ester, 1% vol. oil.
Turpentine ..	130–145	35–40	170–180	Vol. oil 40%, resin (rosin) 60%.

TABLE X

PHYSIOLOGICAL ACTION OF SOME COMMON DRUGS

Opium, and its Chief Alkaloid

Heart.—First slow and strong (effect on vagus nerve and heart muscle) later and especially in large doses, rapid and weak.

Arterial tension.—Increased.

Respiration.—At first slow and deep. Later and especially in large doses, slow, feeble, imperfect (effect on respiratory center in the medulla), finally in lethal doses stopping altogether (cause of death in opium poisoning).

Brain.—Varying in intensity from conditions tending toward reverie, to unconsciousness and finally coma.

Nerves.—Diminished conductivity.

Kidneys.—Sometimes acts as a slight diuretic.

Skin and mucous membranes.—At first dry and warm, later and in larger doses, pallid, cyanose, cold and moist.

Stomach.—Lessened activity.

Intestines.—Peristaltic movements decreased.

Glands.—Secretions decreased (except those of skin).

Pupil.—Contracted.

Metabolism.—Lessened.

Remarks.—Muscles nearly unaffected, temperature lowered.

Cinchona, and its Chief Alkaloids

Heart.—Force and frequency lessened. In lethal doses arrested in diastole.

Arterial tension.—Slightly raised by small doses, lowered by large ones.

Respiration.—Small doses are apparently without effect. Large doses depress.

Brain.—Increased hyperemia.

Nerves.—Disturbs action of end organs.   Diminishes reflexes.

Kidneys.—Eliminated by the urine.   Little change.

Skin and mucous membranes.—Irritant to mucous membranes.

Stomach.—Small doses tone, large doses are apt to nauseate.

Intestines.—Small doses tone.   Acts as an intestinal antiseptic.

Glands.—Small doses stimulate peptic glands.

Pupil.—Unaffected.

Metabolism.—Lessened.

Remarks.—Temperature lowered. Muscle irritant. Anti-amœbic.

Nux Vomica and its Chief Alkaloid

Heart.—Rate increased at first, then slower and stronger.

Arterial tension.—Raised.

Respiration.—Increased, deeper and faster.

Brain.—Nearly unaffected, senses sharp.

Nerves.—Stimulates reflex centers in cord and so greatly increases reflexes.   Paralyzes motor nerves.   Lethal doses cause tetanic spasms.

Kidneys.—No regular effect.   Eliminated with urine.

Skin and mucous membranes.—Slightly irritant.

Stomach.—Tonic, secretion increased.

Intestines.—Tonic, peristalsis increased.

Glands.—Secretions increased.

Pupil.—Slight reaction.

Metabolism.—Increased.

Remarks.—Tonic muscular spasms (tetanic). Stim. of cells of spinal cord. No direct action on muscles.

Coca and its Chief Alkaloid

Heart.—Increased action, rapid.

Arterial tension.—Raised.

Respiration.—Increased and fuller at first, finally in lethal doses paralyzed.

Brain.—Stimulated. Increased cerebration.

Nerves.—Paralyzed. Local anesthetic.

Kidneys.—Secretion increased by small doses.

Skin and mucous membranes.—Blanched, numbed.

Stomach.—Stimulated by small doses. Relieves hunger.

Intestines.—Increased peristalsis.

Glands.—Secretions generally lessened.

Pupil.—Dilated.

Metabolism.—Lessened.

Remarks.—Delays muscular fatigue.

Belladonna and its Chief Alkaloid (also Hyoscyamus, Stramonium, etc.)

Heart.—Slowed at first, then rapid and vigorous, finally in lethal doses weakened.

Arterial tension.—Increased at first, finally diminished.

Respiration.—Increased.

Brain.—Delirium, stupor. Congested.

Nerves.—Motor paralysis of spinal cord: Reflex excitability lessened.

Kidneys.—Acts as a diuretic.

Skin and mucous membranes.—Dry and red. Diminished secretion.

Stomach.—Secretions lessened and finally increased.

Intestines.—Secretions lessened and finally increased.

Glands.—Secretions lessened.
Pupil.—Dilated.
Metabolism.—Lessened.
Remarks.—Temperature elevated.   Muscles not directly
   affected.

Digitalis (also Strophanthus, Convallaria, Apocynum, Squill, etc.)

Heart.—Pulsations slower and stronger (effect on vagus
   and cardiac muscle), finally in lethal doses stopping
   in systole.
Arterial tension.—Increased by stimulating vasomotor
   center, and by increased pressure.
Respiration.—No regular effect, generally increased,
   slightly at first and finally diminished.
Brain.—No regular effect.
Nerves.—Large doses lower reflex excitability (stimula-
   tion of Setchinou's center).
Kidneys.—Diuretic, slightly irritant, the amount of urea
   excreted finally diminishing.
Skin and mucous membranes.—Large doses irritate
   mucous membranes.
Stomach.—Irritant.
Intestines.—Irritant.
Glands.—No regular effect.
Pupil.—No regular effect.
Metabolism.—No regular effect.
Remarks.—Temperature lowered.   Contractility of
   striped muscles lowered.

Aconite and Aconitine

Heart.—Slowed at first, then rapid and weak.
Arterial tension.—Lowered.

Respiration.—Shallow and feeble.   Slower and longer at first.

Brain.—Little effect.

Nerves.—Paralyzes end organs of sensory nerves, also motor nerves themselves.

Kidneys.—Acts as diuretic.

Skin and mucous membranes.—Numbed.   Secretions increased.

Stomach.—Irritant, secretions increased.

Intestines.—Irritant, secretions increased.

Glands.—Secretions slightly increased.

Pupil.—Usually dilated.

Metabolism.—Lessened.

Further remarks.—Relaxed muscles.   Lowered temperature.

Physostigma and its Alkaloids

Heart.—Slow, strong, arrested in diastole after lethal doses.

Arterial tension.—First slightly lowered, then raised.

Respiration.—Small doses have little effect, large doses depress and eventually result in asphyxia.

Brain.—Little effect.

Nerves.—Cord reflexes lowered.

Kidneys.—Excretion slightly increased.

Skin and mucous membranes.—Secretions increased.

Stomach.—Secretions increased.   Irritant.

Intestines.—Secretions increased.   Irritant.

Glands.—Secretions increased.

Pupil.—Contracted.

Metabolism.—Lessened.

Remarks.—Muscles persistently contracted.

Pilocarpus and its Alkaloids

Heart.—Small doses increase action, large doses depress.

Arterial tension.—First lowered, then raised.

Respiration.—Slowed.

Brain.—Little direct effect.

Nerves.—Reflexes at first heightened, then diminished.

Kidneys.—Excretion slightly stimulated.

Skin and mucous membranes.—Secretions increased. Skin red.

Stomach.—Secretion increased. Irritant.

Intestines.—Secretions and peristalsis increased.

Glands.—Secretions increased.

Pupil.—Contracted.

Metabolism.—Excreted partly by skin.

Remarks.—Muscles, especially involuntary ones, contracted.

Hydrastis and Hydrastine

Heart.—Increased force and diminished frequency.

Arterial tension.—Slightly raised at first, then lowered.

Respiration.—Increased depth and frequency. Similar to strychnine.

Brain.—Possibly stimulated.

Nerves.—Stimulates cord and heightens reflexes. Sensory nerves depressed.

Kidneys.—Slight diuretic.

Skin and mucous membranes.—Slightly anesthetic. Promotes healthy secretions.

Stomach.—Increased secretion.

Intestines.—Increased secretions and peristalsis.

Glands.—Increased secretions.

Pupil.—First contracted, then dilated.

Metabolism.—Little effect.

Remarks.—Depresses contractile power of muscles. General muscle poison.

Coffee and Caffein (also Tea, Guarana, Maté, Cacao, etc.)

Heart.—Pulsations stronger. Large doses depress.
Arterial tension.—Slightly increased.
Respiration.—Slightly quickened. Large doses depress.
Brain.—Increases cerebration by stimulation of cerebral cells.
Nerves.—Stimulates motor cells of cord. No action on nerve trunks.
Kidney.—Diuretic.
Skin and mucous membranes.—
Stomach.—Slightly increased peristalsis.
Intestines.—Slightly increased peristalsis.
Glands.—Little effect.
Pupil.—Little effect.
Metabolism.—Diminished.
Remarks.—Stimulates muscle irritability at first, afterward destroying it. Delays muscular fatigue.

Ergot

Heart.—Slowed. Increased by large doses.
Arterial tension.—Raised.
Respiration.—Increased. Ultimately paralyzed.
Brain.—No noticeable effect from small doses. Large disturb.
Nerves.—Little effect. Certain centers stimulated.
Kidneys.—Increased secretion.
Skin and mucous membranes.—Irritant.
Stomach.—Irritant. Contracts. Increased peristalsis.
Intestines.—Irritant. Contracts. Increased peristalsis.
Glands.—Secretions increased.
Pupil.—Dilated.

Metabolism.—Slightly increased.

Remarks.—Temperature depressed.   Contracts involuntary (unstriped) muscle fibre.

Colchicum and its Alkoloids

Heart.—Slightly affected by small, depressed by large doses.

Arterial tension.—Slightly affected by moderate doses.

Respiration.—Slow and deep at first. Lethal doses paralyze.

Brain.—Slight.   Loss of consciousness may result from lethal doses.

Nerves.—Action indirect if at all.

Kidneys.—Diuretic.

Skin and mucous membranes.—Diaphoretic.

Stomach.—Irritant.   Emetic.

Intestines.—Increased catharsis.   Irritant.

Glands.—Secretions increased.

Pupil.—Little effect.

Metabolism.—Little effect.

Remarks.—

Cannabis

Heart.—Slightly quickened, but in animals the intravenous injection generally slows the pulse through stimulation of the inhibitory center and direct action on the heart muscle.

Arterial tension.—Slightly raised.

Respiration.—Increased at first, then diminished.

Brain.—Peculiar intoxication.

Nerves.—Weakly analgesic and anesthetic.   Reflexes first increased, then diminished.

Kidneys.—Slightly diuretic.

Skin and mucous membranes.—Little effect.
Stomach.—Little effect.   Sometimes vomiting.
Intestines.—Little effect.
Glands.—Little effect.
Pupil.—Slightly dilated.
Metabolism.—Slightly diminished.
Remarks.—

Alcohol

Heart.—Small doses stimulate, large ones depress.
Arterial tension.—Raised, although arterioles are dilated.
Respiration.—Small doses stimulate, large ones depress.
Brain.—Small doses may temporarily stimulate, large
    ones disturb.
Nerves.—Reflexes and time reaction may be at first
    slightly quickened, but are quickly depressed.
Kidneys.—Mildly diuretic.
Skin and mucous membranes.—Irritant.   Secretions
    slightly increased.
Stomach.—Small amounts stimulate secretion.
Intestines.—Small amounts may stimulate secretions.
Glands.—Effects variable.
Pupil.—Dilated.
Metabolism.—Lessened.
Remarks.—Temperature reduced.   Muscular weakness
    and finally paralysis.

Chloral

Heart.—Weak and slow at first, weak and rapid later.
Arterial tension.—Lowered.
Respiration.—Weak and slow.
Brain.—Depression of cells, with narcosis.
Nerves.—Reflexes lowered and eventually abolished.

Kidneys.—Slight diuresis.
Skin and mucous membranes.—Irritant.
Stomach.—Irritant.
Intestines.—Irritant.
Glands.—Little effect.
Pupil.—Contracted.
Metabolism.—Lowered.
Remarks.—Temperature reduced.   Muscular paralysis.

Sulfonal and Trional

Heart.—Slightly stimulated.
Arterial tension.—Raised.
Respiration.—Little effect except some slowing with small, paralysis with large doses.
Brain.—Depresses cells of cortex.   Hypnotic.
Nerves.—Diminishes reflexes.
Kidneys.—Slightly diuretic.   Excreted by urine.
Skin and mucous membranes.—
Stomach.—Little effect.
Intestines.—Little effect.
Glands.—Little effect.
Pupil.—Little effect.
Metabolism.—May occasion hematoporphyrinurea when long continued.
Remarks.—

Acetanalid (also Antipyrine, Phenacetin, Lactophenin, etc.)

Heart.—Slower.   Large doses depress.
Arterial tension.—First lowered, then slightly raised.
Respiration.—Little effect from small doses, large doses cause it to be rapid and weak.
Brain.—Slight cerebral stimulant and anesthetic.

Nerves.—Lessens reflexes of cord. Deadens sensory nerves.

Kidneys.—Diuretic.

Skin and mucous membranes.—Diaphoretic (dilation of cutaneous vessels).

Stomach.—Little effect.

Intestines.—Little effect.

Glands.—Little effect.

Pupil.—May be somewhat dilated.

Metabolism.—Little effect.

Remarks.—Lowers temperature, especially when abnormally high, muscle stimulant.

Salicylic Acid and Salicylates

Heart.—Accelerated by small, depressed by large doses.

Arterial pressure.—Increased by small, lowered by large doses.

Respiration.—Accelerated, with dyspnea.

Brain.—Sometimes causes confused ideas, with unusual visual and auditory symptoms.

Nerves.—Spinal centers are first slightly stimulated then depressed.

Kidneys.—Slight diuretic.

Skin and mucous membranes.—Diaphoretic.

Stomach.—Disturbed. Irritant.

Intestines.—Antiseptic.

Glands.—Secretions generally increased.

Pupil.—Little effect.

Metabolism.—Lowered.

Remarks.—Muscles but little affected.

TABLE XI

ATOMIC WEIGHTS OF ELEMENTS

$O = 16$

Element	Symbol and Most Common Apparent Valence.	Atomic Weight.	Melting or Boiling-point, ° C.
Aluminum	Al^{III}	27.1	657.3
Antimony	Sb$^{III \& V}$	120.2	630.5
Argon	A	39.9	− 186.1 (boils)
Arsenic	As$^{III \& V}$	74.96	450 (boils)
Barium	Ba^{II}	137.37	850
Bismuth	Bi^{III}	208	269
Boron	B^{III}	11	3500 (boils)
Bromine	Br^{I}	79.92	63 (boils)
Cadmium	Cd^{II}	112.4	322
Cæsium	Cs^{I}	132.8	26.4
Calcium.	Ca^{II}	40.09	780
Carbon	C^{IV}	12	?
Cerium	Ce$^{II \& IV}$	140.25	623
Chlorine	Cl^{I}	35.46	− 34 (boils)
Chromium	Cr$^{II \& VI}$	52	1515
Cobalt	Co$^{II \& VI}$	58.97	1530
Columbium	Cb ?	93.5	1950
Copper	Cu^{II}	63.57	1065
Dysprosium	Dy ?	162.5	?
Erbium	Er^{II}	167.4	?
Europium	Eu ?	152	?
Fluorine	F^{I}	19	− 187 (boils)
Gadolinum	Gd ?	157.3	?
Gallium	Ga^{III}	69.9	3015
Germanium	Ge ?	72.5	900
Glucinum	Gl ?	9.1	960
Gold	Au^{III}	197.2	1065
Helium	He ?	4	− 267 (boils)
Hydrogen	H^{I}	1.008	− 252.5 (boils)
Indium	In^{III}	114.8	155
Iodine	I^{I}	126.92	114
Iridium	Ir^{IV}	193.1	1950
Iron	Fe$^{II \& VI}$	55.85	1550–1600
Krypton	Kr ?	83	− 152 (boils)
Lanthanum	La^{III}	139	810
Lead	Pb$^{II \& VI}$	207.1	327
Lithium	Li^{I}	7	186
Lutecium.	Lu ?	174	?
Magnesium	Mg^{II}	24.32	633
Manganese	Mn$^{II \& VI}$	54.93	1245
Mercury	Hg^{II}	200	357 (boils)

TABLE XI.—*Continued.*

Element.	Symbol and Most Common Apparent Valence.	Atomic Weight.	Melting or Boiling-point, ° C.
Molybdenum	Mo^{II} & ^{VI} & ^{VIII}	96	?
Neodymium	Nd^{III}	144.3	840
Neon	Ne ?	20	− 243 (boils)
Nickel	Ni^{II} & ^{IV}	58.68	1484
Niobium	Nb^{III}	94	?
Nitrogen	N^{III}	14.01	− 196 (boils)
Osmium	Os^{II} & ^{VI}	190.9	2500
Oxygen	O^{II}	16	− 184 (boils)
Palladium	Pd^{II} & ^{IV}	106.7	1586
Phosphorus	P^{III}	31	44.2
Platinum	Pt^{II} & ^{IV}	195	1780
Potassium	K^{I}	39.10	62.5
Praseodymium.....	Pr^{III}	140.6	940
Radium...........	Ra ?	226.4	?
Rhodium	Rh^{IV}	102.9	2000
Rubidium	Rb^{I}	85.45	38.5
Ruthenium	Ru^{II} & ^{VI}	101.7	1950
Samarium	Sa^{II} & ^{VI}	150.4	?
Scandium	Sc^{III}	44	?
Selenium	Se^{II}	79.2	217
Silicon	Si^{IV}	28.3	1200
Silver............	Ag^{I}	107.88	955
Sodium	Na^{I}	23	97.6
Strontium	Sr^{II}	87.62	900
Sulphur	S^{II}	32.07	115
Tantalum	Ta^{III}	181	2250
Tellurium	Te^{II}	127.5	446
Terbium	Tb ?	159.2	?
Thallium	Tl^{III}	204	302
Thorium	Th^{II} & ^{IV}	232.42	?
Thulium..........	Tm ?	168.5	?
Tin..............	Sn^{II} & ^{IV}	119	232
Titanium	Ti^{II} & ^{IV}	48.1	3000
Tungsten	W^{II} & ^{VI}	184	1700
Uranium	U^{II} & ^{VI}	238.5	800
Vanadium.........	V^{III}	51.2	1680
Xenon	Xe ?	130.7	− 109 (boils)
Ytterbium	Yb^{III}	172	?
Yttrium	Yt^{II}	89	?
Zinc	Zn^{II}	65.37	419
Zirconium	Zr^{II} & ^{IV}	90.6	1500

TABLE XII

COMMONLY USED METRIC AND ENGLISH
EQUIVALENTS

1 meter	= 39.37 inches.
1 liter (cubic decimeter, 1000 cc.)	= 33 fl. oz. 390.6 minims
1 kilogram (w't. of liter of water, 1000 g.)	= 2 lbs. 3 oz. 119.9 gr. avoir.
1 gram	= 15.4324 grains.
1 cubic centimeter (fluid gram)	= 16.23 minims.
31.1035 grams	= 1 oz. troy. or apoth.
28.350 grams	= 1 oz. avoir.
29.5737 cubic centimeters	= 1 fluid ounce.
0.0648 gram	= 1 grain.
0.06161 cubic centimeter	= 1 minim.

APPROXIMATE EQUIVALENTS COMMONLY USED IN PRESCRIPTIONS.

1 milligram (0.001)	= 1/64 grain.
8 milligrams (0.008)	= 1/8 grain.
16 milligrams (0.016)	= 1/4 grain.
64 milligrams (0.064)	= 1 grain.
330 milligrams (0.330)	= 5 grains.
650 milligrams (0.650)	= 10 grains.
1 gram or cubic centimeter	= 15 grains or minims.
4 grams or cubic centimeters	= 1 dram.
5 cubic centimeters	= 1 teaspoonful.
30 grams or cubic centimeters	= 1 ounce.

APPENDIX

Normal Sulphuric Acid. Mix about 30 cc. of ordinary C.P. sulphuric acid with about 900 cc. of distilled water and after cooling to room temperature (22° C.) add water to bring the measure exactly to 1000 cc. and mix thoroughly.

This solution, which is too strong, is standardized as follows: Two or three accurately measured 10 cc. portions are removed by means of a pipette or burette, diluted with distilled water, heated to boiling, and completely precipitated by an excess of barium chloride. After standing for some hours the resulting precipitates are filtered off through an ash-free filter paper, washed until the washings cease to give any cloudiness on the addition of a few drops of sulphuric acid on standing, and dried. Each precipitate is now removed as completely as is convenient to a well-glazed paper, the filters burned in tared crucibles and after cooling again ignited slowly with a few drops of nitric or sulphuric acid. The reserved bulk of the precipitates are now added to their respective crucibles and again ignited, allowed to cool in a desiccator and weighed.

The weight of the barium sulphate found multiplied by 0.4200 will give the amount of actual sulphuric acid in each 10 cc. of the solution, and the remaining measured

portion is now to be diluted as calculated by proportion, until each 10 cc. will contain exactly 0.48675 g., corresponding to 1.1569 g. of barium sulphate. The weight of the precipitates should check closely.

Normal Sodium Hydroxide. Dissolve 50 to 55 g. of stick sodium hydroxide in distilled water and after cooling to room temperature dilute to exactly 1000 cc. Transfer an accurately measured 10 cc. portion of normal sulphuric acid to a flask, dilute with distilled water, add a few drops of phenolphthalein solution as indicator, and gradually add the NaOH solution (which is too strong) to the acid a few drops at a time, shaking during the addition, until a pale pink color just remains. Repeat the titration to insure accuracy and finally dilute the NaOH solution with distilled water so that equal volumes of it and the normal acid will just neutralize each other.

Normal Hydrochloric Acid. Mix 130 cc. of C.P. hydrochloric acid specific gravity 1.158 with distilled water and dilute to 1000 cc. Titrate against the normal NaOH solution and dilute to balance.

Normal Oxalic Acid. Weigh 63 g. of pure recrystallized oxalic acid (containing two molecules of water and crystallization) dissolve in distilled water and make up to 1000 cc.

This is generally assumed to be near enough to the correct strength but may be titrated against the normal NaOH solution if desired.

Other Normal Acid Solutions may be similarly prepared.

Normal Alcoholic Potassium Hydroxide. Dissolve about 65 g. of stick potassium hydroxide in alcohol which has been purified by distillation over silver nitrate, and dilute with the same purified alcohol to 1000 cc.; standardize to balance against normal sulphuric acid.

Tenth or Deci-Normal Iodine. Weigh 12.59 g. of iodine which has been carefully purified by resublimation, dissolve in about 300 cc. of distilled water by the aid of 18 or 20 g. of potassium iodide and dilute to 1000 cc. It should check N/10 silver nitrate.

Tenth Normal Sodium Thiosulphate. Dissolve about 30 g. of crystallized sodium thiosulphate in water and dilute to 1000 cc. at room temperature. Standardize to balance against tenth normal iodine, using toward the last a few drops of starch solution as indicator.

Tenth Normal Potassium Dichromate.. Weigh 4.8713 g. of pure powdered crystals of potassium dichromate which has previously been dried at 120° C. to constant weight, dissolve in distilled water and dilute to 1000 cc.

Tenth Normal Potassium Permanganate. Dissolve 3.3 g. of potassium permanganate in 1000 cc. of water, boil for five minutes, close the flask with a cotton plug, allow to stand for two or three days, decant the clear solution, titrate against tenth normal oxalic acid solution and dilute to balance. In the titration one or two cubic centimeters of strong sulphuric acid should be added to 10 cc. of the tenth normal acid diluted with a little hot distilled water, and the permanganate run in a few drops at a time until the first permanent pale pink color remains two minutes.

Tenth Normal Silver Nitrate. Dissolve 16.869 g. of the purest silver nitrate crystals which have been dried to constant weight at 130° C. before weighing, in distilled water and dilute to 1000 cc. at room temperature.

Tenth Normal Sodium Chloride. This contains 5.806 g. of C.P. salt in each 1000 cc., but should be standardized against the silver nitrate unless the former is known to be pure.

Fehling's Cupric Tartrate Solution. *A.* Dissolve 34.666 g. of pure crystallized copper sulphate in water and make up to 500 cc. *B.* Dissolve 173 g. of sodium and potassium tartrate and 75 g. of potassium hydroxide in water and make up to 500 cc. For use mix equal volumes of solution *A* and *B*, when each cubic centimeter of the mixture is equal to 0.005 g. of glucose.

Ammonium Molybdate Solution. Dissolve 10 g. of molybdic acid in 42 cc. of 8% ammonium hydroxide. When wanted for use one part of this is to be mixed with three parts of 30% nitric acid, specific gravity 1.10.

Magnesia Mixture. Dissolve 10 g. of magnesium sulphate, 20 g. of ammonium chloride and 40 cc. 10% ammonia in water to make 100 cc.

Hubl's Iodine Solution. *A.* 6% mercuric chloride in alcohol. *B.* 5% iodine in alcohol. For use equal volumes of these are mixed and allowed to stand in excess over a weighed amount of fat for several hours, potassic iodide is then added with a little chloroform and the excess of iodine titrated with tenth normal sodium thiosulphate.

Ammonium Sulphide. Saturate 10% ammonium hydroxide with hydrogen sulphide gas and mix three volumes of this solution with two volumes of 10% ammonium hydroxide.

Indicators for acidimetry and alkalimetry:

> Phenolphthalein, 1% in 50% alcohol.
> Methyl orange, 1% in 50% alcohol.
> Cochineal tincture, 5% in 50% alcohol.

Besides these there will be needed normal and basic lead acetate solutions (25%), ferric chloride, barium nitrate, barium chloride, barium hydroxide, ammonium carbonate (containing some ammonium hydroxide),

potassium ferrocyanide, potassium sulphocyanide, potassium or sodium nitrite, calcium chloride, ferrous sulphate, calcium sulphate, potassium or ammonium acetate, potassium iodide, potassium chromate, ferrous sulphide for generating hydrogen sulphide, silver nitrate, sodium hydrogen phosphate, pure iron wire, copper foil, copper oxide, arsenic free zinc, saturated solution of picric acid, 5% gold chloride, 5% platinic chloride, 5% mercuric chloride, Mayer's solution (mercuric chloride 1.344 g., potassium iodide 5 g. and water to 1000 cc.), alcohol, chloroform, benzene (C_6H_6), petroleum ether, ether, ethyl acetate, methyl alcohol, phenylhydrazine, acetic anhydride, acetyl chloride, stannous chloride, oxygen gas, Nessler's solution, phosphomolybdic acid, phosphotungstic acid, bromine, potassium bismuth iodide, potassium cyanide, sodium peroxide, lead chromate, acid mercuric nitrate, potassium permanganate, potassium dichromate, etc.

INDEX